

1981

## Purification of the Chelating Polymer Poly-5-Vinyl-8-Hydroxyquinoline

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PURIFICATION OF THE CHELATING POLYMER

POLY-5-VINYL-8-HYDROXYQUINOLINE

BY

BRUCE A. MARTIN

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

MASTERS OF SCIENCE

IN

CHEMISTRY

UNIVERSITY OF RHODE ISLAND

1981

MASTERS OF SCIENCE THESIS

OF

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1981

## THESIS ABSTRACT

Preconcentration of solutions by the methods of precipitation and the related technique of co-precipitation generally involve the addition of organic chelating agents and the adjustment of pH through addition of buffer solutions. When dealing with large sample volumes, the analyst is not usually concerned with the possibility of also adding low levels of heavy metal contaminants along with these chemicals. However, when dealing with small sample volumes and in situations where duplicate analyses are not possible all sources of contamination including the precipitating agent and buffer solutions must be examined.

Sample solutions of the chelating polymer poly-5-vinyl-8-hydroxyquinoline (PVO) were prepared and subjected to purification utilizing the technique of constant potential electrolysis (CPE). Differential pulse polarography (DPP) and atomic absorption spectroscopy (AAS) analysis were performed before, during, and after electrolysis to visually and quantitatively follow the decrease in lead contamination of the polymer solution.

The procedure was successful in removing approximately 96% of the initial lead contamination from the sample solution. Ultraviolet work performed indicates that purification of the solution proceeded without any adverse effects on the integrity of the organic precipitant.

Acids and base used in the preparation of the buffer solutions were purified by two different distillation methods and will also be discussed.



### ACKNOWLEDGEMENTS

I would like to thank Dr. James L. Fasching for his assistance and patience throughout the long years I spent in his graduate laboratory here at the University of Rhode Island. Although many times I had a tendency to stray away from the direction of my ultimate goal, you always found a way to bring me back on course. It was always what you did not say to me that I heard the loudest!

I would also like to thank some of the other members of the Chemistry department for personal encouragement, professional ability, and the use of much of their time and equipment; Dr. Chris Brown, Dr. Phyllis Brown, Dr. Bruno Vittimberga, and Dr. Louis Kirschenbaum. A special thanks is extended to Dr. Ken Force'. Your abilities as a teacher and as a scientist are commendable.

I also wish to acknowledge some of my fellow graduate students both past and present. To name but a few; John Rossell, Marty Hughes, Roy Heaton, Dave Stout, Cliff Wiesel, Marie Sabo, Mark Ahmadjian, Gene Franklin, JoAnn Prezwosnik Woods, and last but not least, Jerry Ortolano of the Pharmacology department.

In addition I would like to thank my family for their love and support shown me throughout these many trying years in graduate school. My father, Walter A. Martin, and mother, Virginia Martin, always believed in me and helped me as best they could even when times were the worst. A thanks to my brother Ron, sister Pat, and especially to my kid brother

Stephen for having put up with my often disagreeable moods. You have also been truly sympathetic and encouraging and I am proud to call you brothers and sister.

Lastly, but certainly not the least, I wish to thank my wife and love Diane. You define the words contentment and happiness for me.

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For my son Corey...

May your head always stay above  
the water too.

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## INTRODUCTION

The purification of solutions employed in analysis, i.e., removal of the elements to be determined from auxiliary solutions such as buffers, indicators, water, etc. is accomplished extensively by the method of chelate extraction. In the determination of aluminum as the 8-hydroxyquinolate by the fluorimetric-extraction method (R62), the buffer solution used (ammonium acetate-hydrochloric acid) was first purified by extraction with a chloroform solution of 8-hydroxyquinoline. The extraction was continued until the extract was no longer fluorescent and then the buffer solution was washed with purified chloroform.

In the determination of zinc in foodstuffs (A48) by the dithizone method, zinc was first removed from a solution of trisubstituted sodium citrate. A sample of the salt was dissolved in water and made alkaline with ammonia. The solution was shaken with successive portions of 0.1N dithizone in chloroform until the last extracts remained green. A little citric acid was then added and the solution was shaken with a few portions of chloroform until the last portions of the extract became colorless (removal of the dithizone). Other reagents have been purified by dithizone in a similar procedure (A54, P42).

More generally, chelating agents are used to concentrate rather than to purify. Zlatkis, et al. demonstrated the efficiency of a chromatographic column packed with the polymer



poly-(triaminophenol-glyoxal) supported on Chromsorb W to chelate copper (Z70). An aqueous sample volume was chosen so that 1-10 ug of copper was passed through the column. The column was then washed and eluted with 0.5N hydrochloric acid. The eluent was transferred to a separatory funnel and the copper was concentrated into methyl isobutyl ketone (MIBK). This was accomplished by use of the chelating agent ammonium pyrrolidine dithiocarbamate (APDC). Krishnamurty, et al., (K77) prepared tris(pyrrolidine dithiocarbamate) cobalt (III) chelate matrix to preconcentrate lead from aqueous solutions. This chelating matrix has also been reported to be particularly well suited for preconcentrating trace metals in seawater (B75A). Lo, et al., (L77) preconcentrated mercury, gold, and copper in seawater using diethyldithiocarbamate.

Chelating agents of many molecular configurations have been reported used in conjunction with the concentrating procedures mentioned here; solvent extraction (B69, A76) and ion exchange (L64, C66, B73, R68A, L75B, L75A, G76). However, of interest to this work is the chelating polymer poly-5-vinyl-8-hydroxyquinoline (PVO) first reported by Buono, et al., (B75B) as a precipitant for trace metals from seawater. This polymer was developed by Vijayaraghaven (V68) and possesses all the chelating properties of 8-hydroxyquinoline, a reagent used for many years to preconcentrate trace metals by coprecipitation (F37, M47, H53).

In precipitation and coprecipitation methods of

concentrating trace elements, the insoluble metal complexes are, in most cases, analyzed directly. It seems logical that if the amount of chelating agent added to the sample is not kept to a minimum, that extreme contamination of the sample could result. Even if the added precipitant contains very small amounts of the elements of interest, the analyst should be aware of the impurity levels present.

This work deals with the use of a separation technique not based on extraction or ion exchange procedures for the removal of metallic impurities in the chelating polymer PVO. By electrochemically reducing the ions in a solution of the PVO, purified reagent is achieved.

Polarography is a branch of electroanalytical chemistry which deals with the measurements and interpretation of current-voltage relationships. This study is conducted upon a solution undergoing electrolysis between a pair of electrodes. J. Heyrovsky in 1921 first demonstrated the reduction of inorganic ions at a dropping mercury electrode (DME). In so doing he performed the earliest polarographic measurements. In 1925, Shikuta (S25) succeeded in reducing nitrobenzene at a DME and simultaneously gave birth to organic applications of Heyrovsky's new method of analysis.

Widespread and accepted application of this electroanalytical method did not come about until ten years later. At this time, Ilkovic derived his famous equation for explaining the pertinent relationships involved in polarographic analysis. This equation, possessing his name,



initiated better understanding of the technique and increased its use for studying both organic and inorganic pollutants.

Today, the use of polarographic and related techniques are found in almost every well equipped analytical laboratory dealing with both heavy metal and organic pollutants. In meeting the needs for increased environmental pollution studies and in striving for higher sensitivities to detect the trace levels of impurities found in environmental samples, electrochemical techniques have approached and in some cases surpassed the abilities of other methods of analysis. With the advent of differential pulse polarography (DPP) (E70) and the other stripping techniques (M72B,M73, R73,R74,M74), the scope of polarography has broadened into the region of true trace analysis.

Bosserman, et al., (B78) employed DPP along with a preconcentration procedure utilizing 8-hydroxyquinoline (oxine) to determine molybdenum at the parts-per-billion level (ppb). On comparison of this method to more elaborate analysis techniques such as instrumental neutron activation (INAA), or X-ray fluorescence he indicated compatible accuracy but shorter analysis times, lower costs, and the ease of this method in a variety of applications. Hasebe, et al., (H75) utilized DPP to determine some carcinogenic nitosamines. Studies on the prevalence, toxicity, and significance to public health of these compounds required an analysis at the 5-10 ng/g level. This study indicates that DPP was chosen over other methods (spectrophotometry,

gas-liquid chromatography, gas chromatography-mass spectrometry) because of time, expense, and in the latter comparison the limited application to volatile compounds was stated.

The determination of trace concentrations of metals has also been carried out using the method of anodic stripping voltammetry (ASV). This technique differs from the polarographic techniques previously stated in that the solution upon which it is being applied is unstirred. The electrode at which reduction is occurring is stationary and a double layer is allowed to form. Sinko (S74) analyzed copper, cadmium, lead, and zinc in natural waters by ASV. He was able to quantitate cadmium and lead at the  $10^{-8}\text{M}$  levels and copper and zinc ions at concentrations of  $2 \times 10^{-8}\text{M}$ . Lower concentrations of copper and zinc ions could not be determined although well shaped current-voltage curves were obtained. The copper and zinc ion concentrations in the supporting electrolyte (approximately  $10^{-8}\text{M}$ ) was reported as being the cause for this lower analysis limit. Kublik (K61) performed similar work on drinking water using ASV. Chau (C74A) in a study to determine labile vs. strongly bound metals in lake water analyzed for zinc, cadmium, lead, and copper. They were able to report values of less than 10 ppb along with standard deviations of from 1.6 to 10%.

It can be deduced from the levels of sensitivities obtained by these two methods of analysis, DPP and ASV, that great care must be taken to secure or prepare reagents



sufficiently free from the substance being determined to provide for satisfactory low blanks. Robertson (R68B) has analyzed a variety of solvents, reagents, and other materials normally encountered in trace elemental analysis. Table I indicates the levels of contamination found in a number of chelating agents as well as those reagents pertinent to this work. Although lead is not presented (analysis performed by INAA) the reader should be able to grasp the extent to which contamination occurs. Most purified solvents and reagents contain trace elements at concentrations high enough to pose serious questions of low level analysis results, especially when substantial amounts of these materials are being used in preconcentration or chemical separation procedures. Robertson (R68B) indicates that chelating agents overall contain significant concentrations of many metals, notably iron, zinc, copper, silver, antimony, and cobalt.

Using the stripping technique of constant-potential electrolysis (CPE), Meites (M55) removed the interfering zinc contamination from 2M sodium hydroxide solution. He was also able to purify ammoniacal ammonium chloride solution from concentrations of nickel and zinc, citrate solution from iron, and alkali and alkaline earth metals from tetraethylammonium hydroxide solution. Copeland and Osteryoung (C74B) used exhaustive electrolysis to purify supporting electrolytes before examining the copper-zinc intermetallic interferences found upon ASV analysis of solutions

\* Table (I)

A Few Trace Element Contaminants Concentrations  
Found in Laboratory Reagents and Organic Precipitants.  
(Samples analyzed by Neutron Activation Analysis)

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\* Table partially reproduced from a paper by

Robertson, D.E. :Role of Contamination in Trace Element  
Analysis of Sea Water. Anal. Chem. 40, 1067, (1968).

Table (I)

	Concentration (ng/ml)							
	<u>Zn</u>	<u>Fe</u>	<u>Sb</u>	<u>Co</u>	<u>Cr</u>	<u>Sc</u>	<u>Cs</u>	<u>Ag</u>
Nitric acid (1)	13	~ 2	~ 0.03	0.018	72	0.0007	< 0.01	~ 0.24
Hydrochloric acid (1)	22	~ 1	0.20	0.09	1.1	0.002	< 0.002	0.1
Ammonium hydroxide (1)	2.3	< 0.1	< 0.006	~ 0.009	< 0.04	< 0.0003	< 0.002	< 0.1
Dithizone (m)	1150	< 7000	0.8	1.2	< 2000	0.15	10	< 10
Sodium diethyl- dithio-carbamate (m)	40	< 600	42	0.56	U.M.	0.02	< 1	< 10
Sodium hydroxide (1)	< 20	< 900	0.32	5.5	60	0.30	0.69	< 0.2
Potassium hydroxide (m)	1250	2700	1.8	1.7	< 10	0.04	< 0.01	66
8-Hydroxyquinoline (dd) U.M.	U.M.	U.M.	1210	U.M.	U.M.	0.14	U.M.	< 10
8-Hydroxyquinoline (ee) 370	5700	2.1	1.8	U.M.	0.06	< 0.1	< 0.8	
8-Hydroxyquinoline (ff) < 100	1000	6.0	< 0.4	< 50	< 0.04	< 0.4	< 0.40	
8-Hydroxyquinoline (z) < 40	< 100	< 0.2	< 0.2	< 50	< 0.02	< 0.1	< 1	

(1) Baker and Adamson, C.P. Reagent

(ee) A.D. MacKay, Co.

(m) Baker Analyzed Reagent

(ff) J.T. Baker Chemical Co.

(dd) Fisher Scientific Certified Reagent

(z) Eastman Organic Chemicals

\* U.M. (unable to measure because of interfering radionuclides)

containing these two elements. Catherino and Meites (C64) employed electrolysis as a method of purifying sodium tartrate solution from the interference of a variety of contaminant elements. Copeland and Skogerboe (C74C) report that with concentrations of supporting electrolytes in sample solutions in the range of 0.05M to 0.5M, purification of all reagents by constant-potential electrolysis or a similarly effective method of removing the interfering ions is often required. They make the point quite clear by stating that such a procedure is mandatory for accurate analysis results at concentrations approaching  $10^{-9}M$ .

It is with this fact in mind that a procedure for the electrolysis and subsequent purification of the chelating polymer PVO was undertaken.



## EXPERIMENTAL

### Instrumentation

Differential pulse polarograms were obtained by use of a Princeton Applied Research Model 364 Polarographic analyzer using a three electrode system and a Heath Schlumberger Model SR-207 XY recorder. A Princeton Applied Research Model 1746 drop timer was connected to the polarograph and used to insure reproducible drop size.

The reference electrode used was a Corning (cat#476000) calomel fiber junction electrode. The auxiliary electrode employed was a Corning (cat#476060) platinum electrode.

Atomic absorption work was performed with a Jarrel Ash Model 850 microprocessor controlled spectrometer equipped with a Jarrel Ash System (I) data translator and an FLA 100 graphite furnace. An Omniscribe dual channel recorder was used to record the data.

The electrolysis was performed using the potentiostat described in Appendix B. The instrument was designed and built specifically for this electrolysis procedure. The ultraviolet data presented was obtained using a Bausch & Lomb Spectronic 505 scanning spectrophotometer.

### Electrochemical Cell

The electrochemical cell used is shown in Fig. 1. It consists of 600 ml glass beaker with two drain taps together with teflon stopcocks attached near the bottom of the beaker. One tap is situated low enough to facilitate

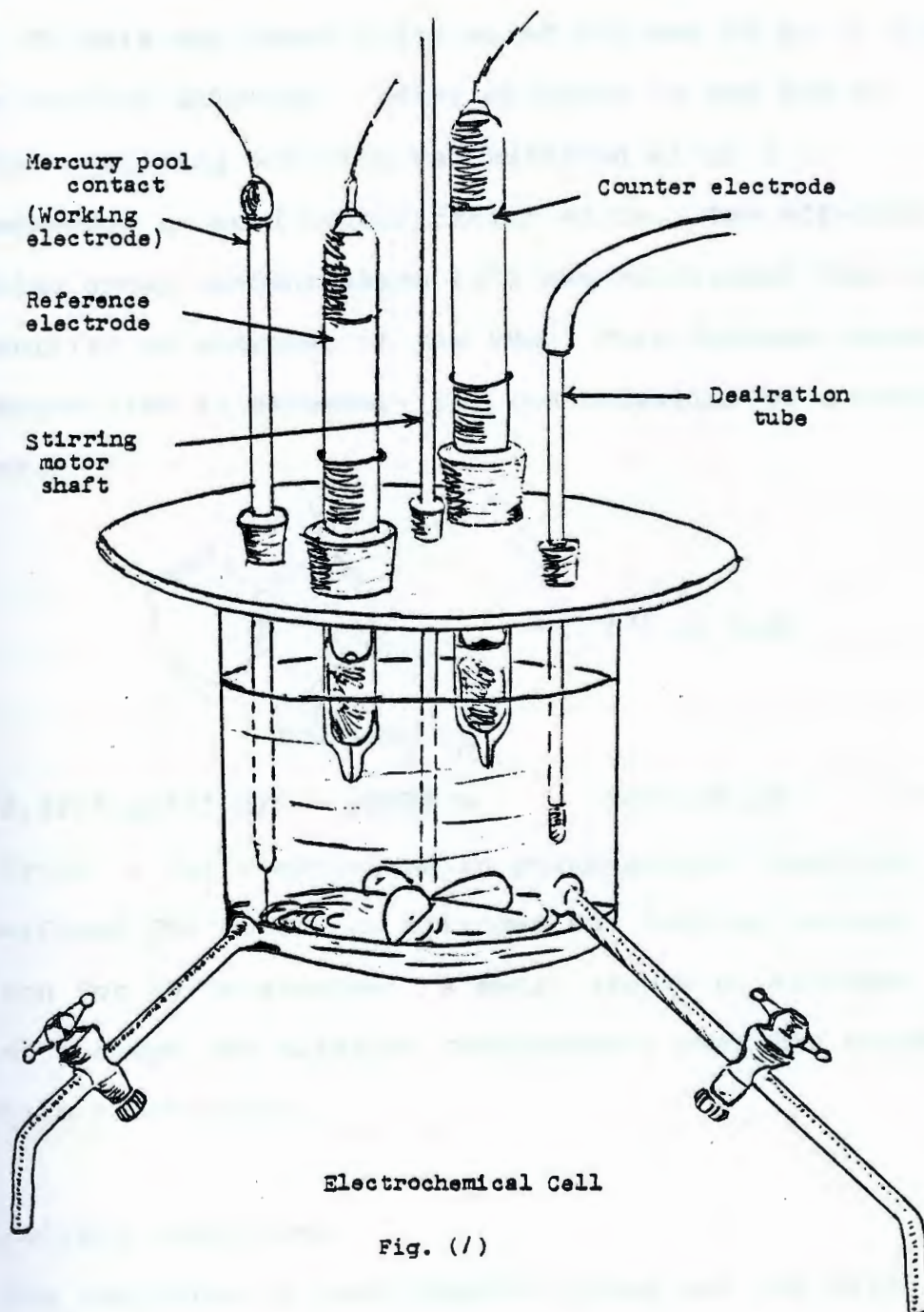
complete removal of the mercury pool working electrode while the other tap is located approximately 1.5 cm higher and on the other side of the cell. This tap is for easy recovery of the electrolyzed solutions.

The cell top is constructed of clear 1/8" thick plexiglass with access ports for insertion of the calomel reference electrode, the auxiliary electrode, the glass stirring shaft, a nitrogen bubbler for deairation of the solutions, and a glass encased platinum wire for contact to the mercury pool working electrode. When differential pulse polarography is being performed the platinum contact is removed and the DME is inserted through this latter port.

#### Chemicals

The salt bridges for the calomel reference electrode and the auxiliary platinum electrode were prepared using Calbiochem brand agar (Calbiochem-Behring Corp., Ca). The mercury used both for the DME and the working electrode pool was of the triply distilled type from ESR (Eastern Smelting & Refining, Mass.) and was purified by the procedure discussed later in this text. All other materials such as the ammonium nitrate used as the electrolyte in the agar salt bridges, the acetic acid used to dissolve the PVO, the ammonium acetate used to prepare the buffer solution, the ammonium metavanadate, zinc, and ammonium hydroxide used in constructing the oxygen scrubbing tower were ordinary reagent grade chemicals.

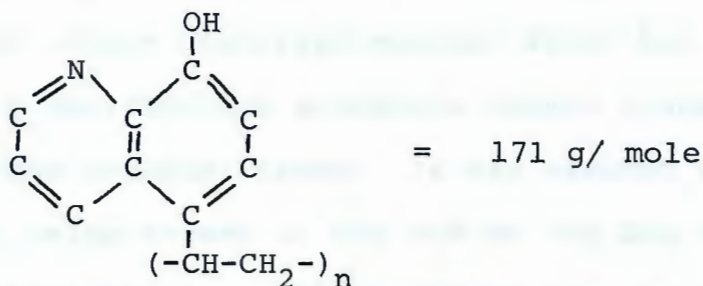
Fig. (1) The Electrochemical Cell design showing the configuration of the stirring motor shaft, the deairation tube, the mercury pool contact, and the auxillary and reference electrodes.





## Sample Preparation

Into a clean leached 250 ml polyethylene volumetric flask was poured 73.5 ml of concentrated purified acetic acid. To this was added 427.5 mg of PVO and 25 ml of 0.245M sodium acetate solution. After dilution to the 250 ml mark the resulting solution was buffered at pH 2.5 and possessed an acid concentration of 5M. The effective chelating group concentration ( $Q^-$ ) was calculated from the availability of nitrogen in the PVO. This follows since a nitrogen atom is necessary for the formation of a chelate complex.



$$0.4275 \text{ g} / 171 \text{ g/m} = .0025 \text{ m} \qquad .0025 \text{ m} / 0.25 \text{ l} = .01 \text{ M}$$

Prior to differential pulse polarographic analysis of the buffered PVO solution, nitrogen was bubbled through the solution for 25-30 minutes. A small stream of nitrogen was bubbled through the solution continuously over the course of an entire electrolysis.

## Electrolysis Conditions

The reduction in lead concentrations and the data presented here were obtained after exhaustive electrolysis of the solution. Generally, the best results were obtained

after approximately 15 to 17 hours of electrolysis. The potential of the electrochemical cell was set at -0.80 volts vs. Standard Calomel Electrode (SCE) which was well cathodic of the reduction potential of lead.

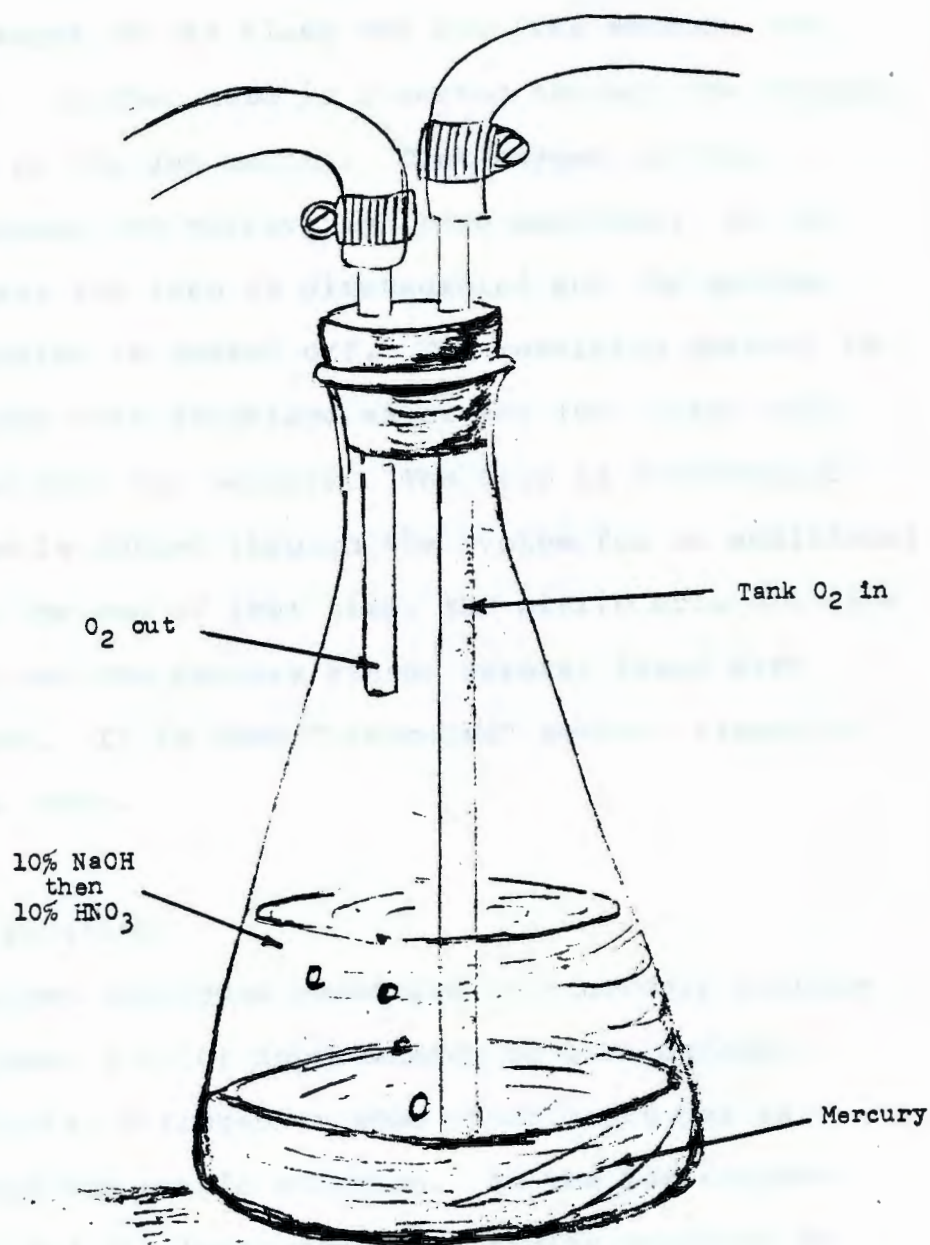
### Mercury Purification

All of the mercury used in conjunction with the DME as well as the mercury used as the working electrode pool was subjected to a purification procedure before use. Due to the low levels of impurities being analyzed polarographically, the instrument sensitivity was greatly increased. It was found that triply distilled mercury which had not been subjected to a purification procedure caused transients to appear in the recorder trace. It was assumed that the mercury drops being formed at the end of the DME capillary were forming irregularly. This could be brought about through non-uniform surface tension of the droplets caused by minute amounts of either organic impurities or amalgams of the mercury with metallic impurities.

To alleviate this problem, the mercury was prepurified by the method reported by Meites (M59) and by Whitnack (W69). This procedure is comprised of filtering the mercury first through a filter paper which has a small pin hole in the bottom of the filter cone. This filtering removes excess organic "scum" from the mercury. The mercury is then poured into a flask and two inches of 10% sodium hydroxide is poured over the top. The purification set-up is shown in Fig. 2.

Fig. (2) The Mercury Purification Trap showing the inlet tube of tank oxygen and the gas outlet tube. A layer of 10% NaOH is poured over the mercury, purging continues for 24 hrs., the mercury is rinsed, and a 10% HNO<sub>3</sub> solution is added. The purging is then continued for an additional 24 hrs., the mercury is rinsed again, then "pin-holed".





Mercury Purification

Fig. (2)

The flask is fitted with a two holed rubber stopper through which a glass tube inlet is inserted. This inlet then extends the length of the flask and into the mercury pool at the bottom. Another tube is inserted through the stopper and functions as the gas outlet. Tank oxygen is then bubbled up through the mercury and base solution. At the end of 24 hours, the trap is disassembled and the sodium hydroxide solution is poured off. The remaining mercury is washed 2-3 times with deionized water and 10% nitric acid is then poured over the mercury. The trap is reassembled and the oxygen is purged through the system for an additional 24 hours. At the end of that time, the nitric acid solution is poured off and the mercury rinsed several times with deionized water. It is then "pin-holed" several times to remove excess water.

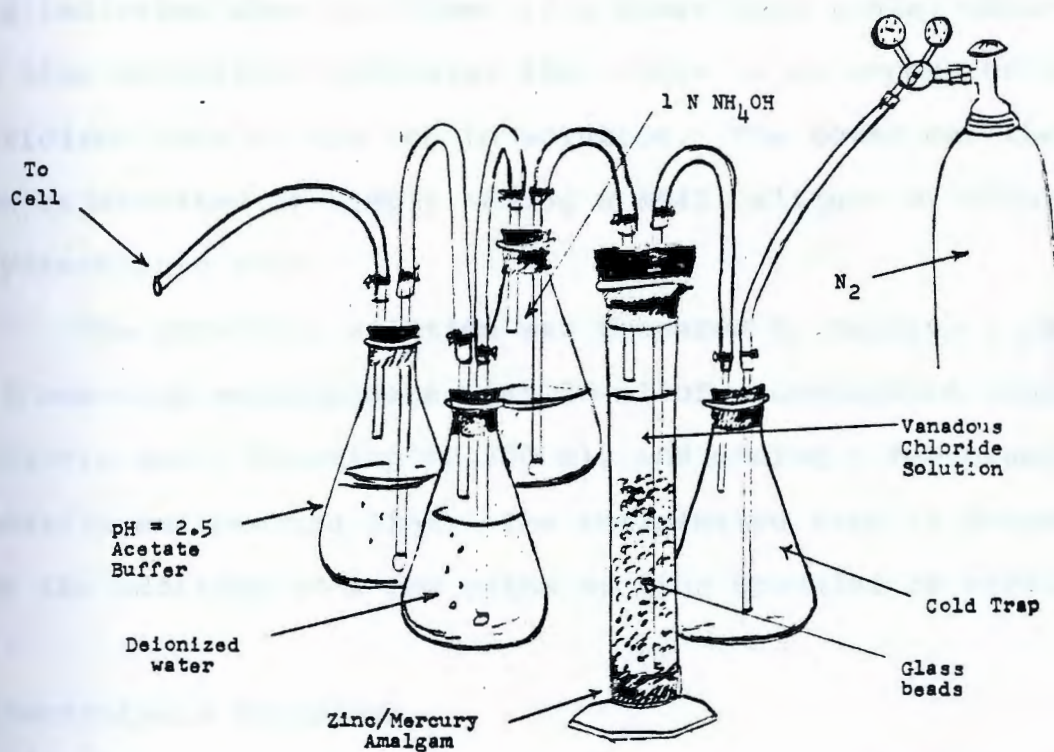
#### Nitrogen Purification

Since oxygen undergoes reduction at a mercury cathode and thereby poses a major interference to polarographic forms of analysis, nitrogen or some other inert gas is bubbled through the sample solution. At the low concentration levels and the instrument sensitivity employed to detect trace metals, commercially-obtained pre-purified oxygen-free nitrogen still contains sizable amounts of oxygen. For this reason a pretreatment of the nitrogen was necessary.

The purification system consists of vanadous chloride

Fig. (3) The Nitrogen Scrubbing System showing the traps employed to remove traces of oxygen from the tank nitrogen. Figure indicates the positioning of the cold trap, trap containing the vanadium scrubbing solution, trap of 1N vanadium solution, trap of deionized water, and the trap of a matching buffer solution to that in the cell.





Nitrogen Scrubbing System

Fig. (3)

solution above heavily amalgamated zinc. Reagent grade tank nitrogen is bubbled up through a column of this solution forming the V(III) ion. The amalgamated zinc re-reduces the vanadium solution so that the column is continually rejuvenated, Fig. (3).

The effectiveness of the oxygen scrubbing is maximized when there is an abundance of V(II) ions in the solution as indicated when the tower is a clear deep violet color. A blue coloration indicates that there is an excess of the oxidized form of the ion in solution. The tower can then be rejuvenated by simply adding a small aliquot of dilute hydrochloric acid.

The scrubbing solution was prepared by boiling 2 gms of ammonium metavanadate with 25 ml of concentrated hydrochloric acid, diluting to 200 ml, and adding a few grams of heavily amalgamated zinc. The amalgamated zinc is prepared by the addition of a few grams of zinc granules to mercury.

#### Electrolysis Procedure

Prior to each constant-potential electrolysis (CPE), a differential pulse polarogram was taken on the solution. After several washings with tap water and several more washings with deionized water, the cell was secured to a ring stand by means of a beaker clamp. Approximately 200 ml of the solution to be electrolyzed was then poured into the cell. The stopcocks were then opened slightly to permit escape of trapped air in the drain arms. The plexiglass top

of the cell was positioned and each of the entrance ports were plugged with a solid cork. This was done to assure minimal leakage of nitrogen purge gas from the cell during deairation. The tip of the pipet from which flowed the purified nitrogen was placed into its respective port in the top of the cell and positioned about 1 cm from the floor of the cell. After approximately thirty minutes of deairation the solid corks were removed from the plexiglass cover and replaced by the plugs containing the reference electrode, auxiliary electrode, and DME. The nitrogen bubbler was removed from the solution, the pipet removed from the end of the hose leading to the scrubbing towers, and the hose itself replaced into the port for solution deairation. This afforded a good flow of nitrogen over the solution surface and maintained an inert atmosphere within the cell.

The mercury reservoir was raised to predetermined and reproducible height over the cell and a visual check was made that mercury was indeed flowing from the tip of the capillary. The drop timer was then connected, the polarograph switched to scan, and a differential pulse polarogram was recorded.

At the conclusion of the scan the polarograph was switched to standby and the drop timer was disconnected. The mercury reservoir was lowered and a visual check again was made to assure that no mercury was flowing from the capillary. The DME was then removed from the cell by



loosening the beaker clamp holding the cell to the ring stand and sliding the assembly down and away from the drop timer. The exposed tip of the capillary was then positioned to one side of the cell and immersed in a solution of dilute nitric acid. The polarograph was switched to off and the electrodes were disconnected from the drop timer.

The top of the cell was lifted just high enough so mercury could be poured into the bottom of the cell. Enough mercury was poured into the cell to cover the bottom of the beaker. The top was repositioned and a plug containing the connection to the mercury pool was fit into the DME port. This connection was a platinum wire sealed into soft glass with an inner mercury pool-wire lead junction. In the center of the cell top was positioned a plug for the glass stirring shaft. The tip of the shaft was immersed into the solution and to a depth so as to just touch the mercury pool. Constant stirring during the electrolysis procedure prohibited a "double-layer" from forming at the mercury pool cathode-solution interface and thereby afforded a continuous supply of reducible lead ions to this electrode.

All of the electrodes were then connected to the potentiostat described in Appendix B. The potential was set to -0.80 volts vs. SCE., a potential cathodic of the reduction potential for lead. Electrolysis was begun when the potentiostat was switched to on and the stirring motor was started.

Fig. (4) UV absorption profile of the polymer  
dissolved in a pH = 2.5, 5 M acetate buffer  
solution prior to electrolysis.



# UV Absorption of Polymer Before Electrolysis

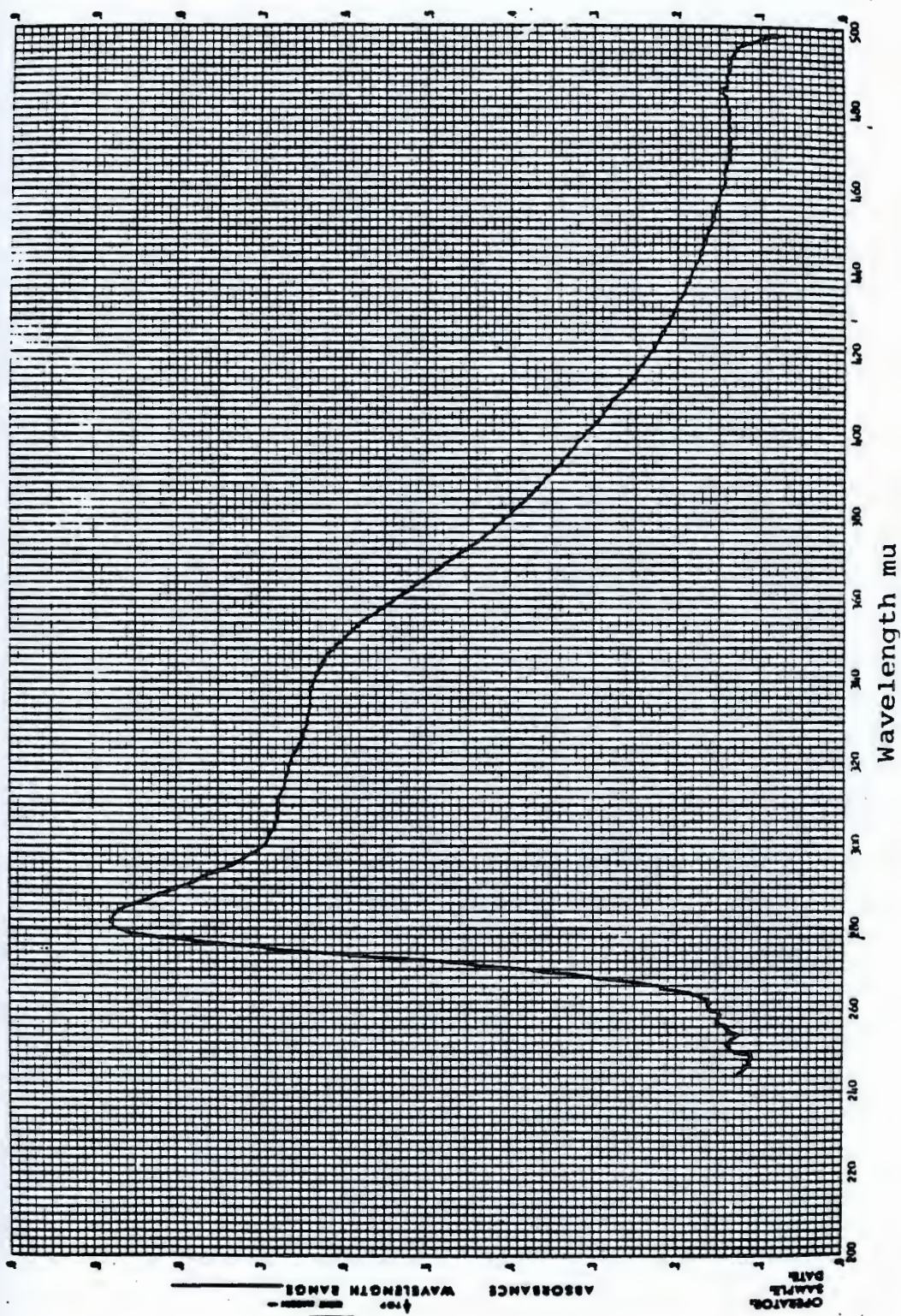
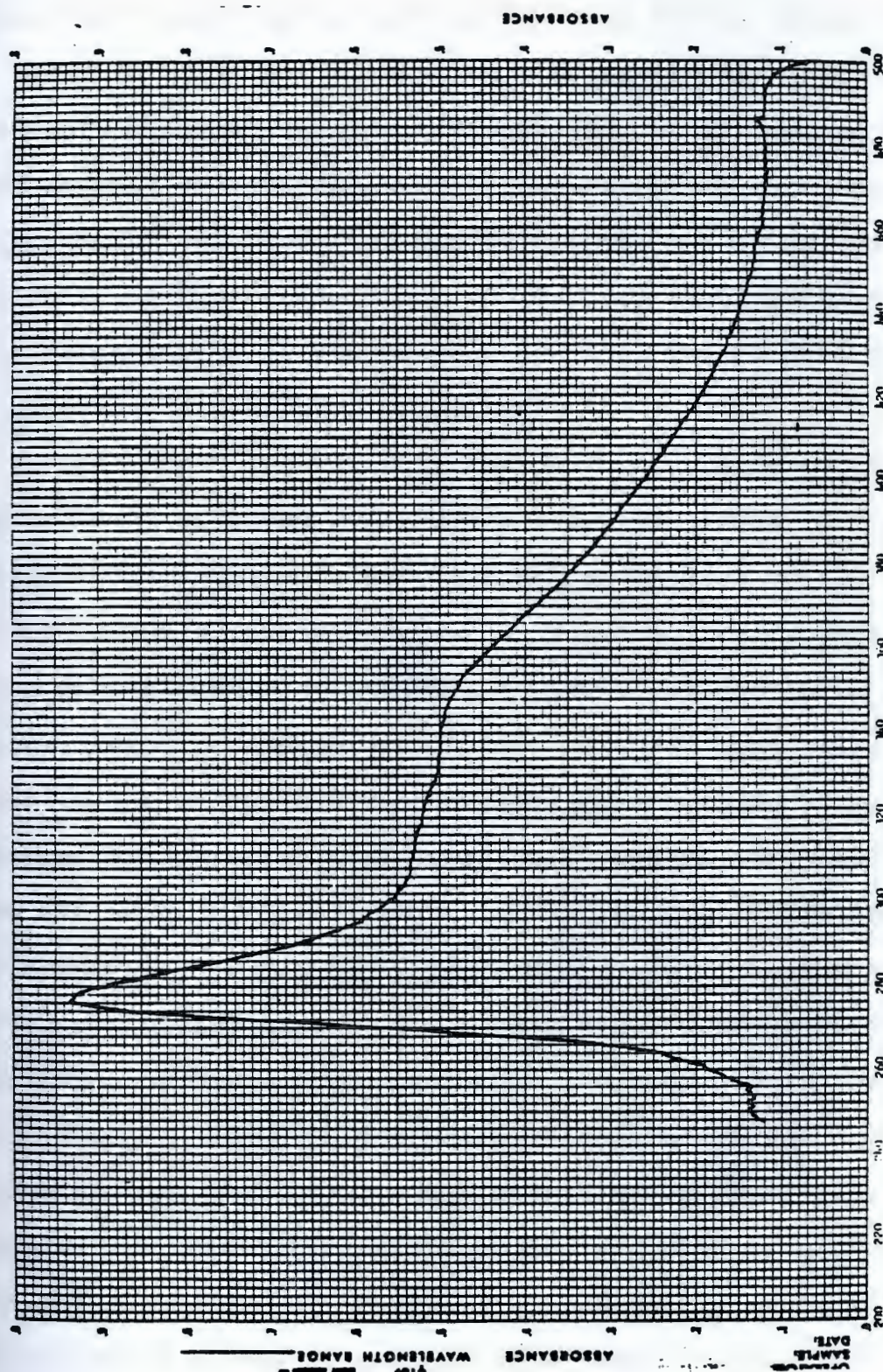


Fig. (4)



Fig. (5) UV absorption profile of the polymer dissolved in a pH = 2.5, 5 M acetate buffer solution after 15 hrs. of electrolysis.

# UV Absorption of Polymer After Electrolysis



Wavelength  $\mu$

Fig. (5)



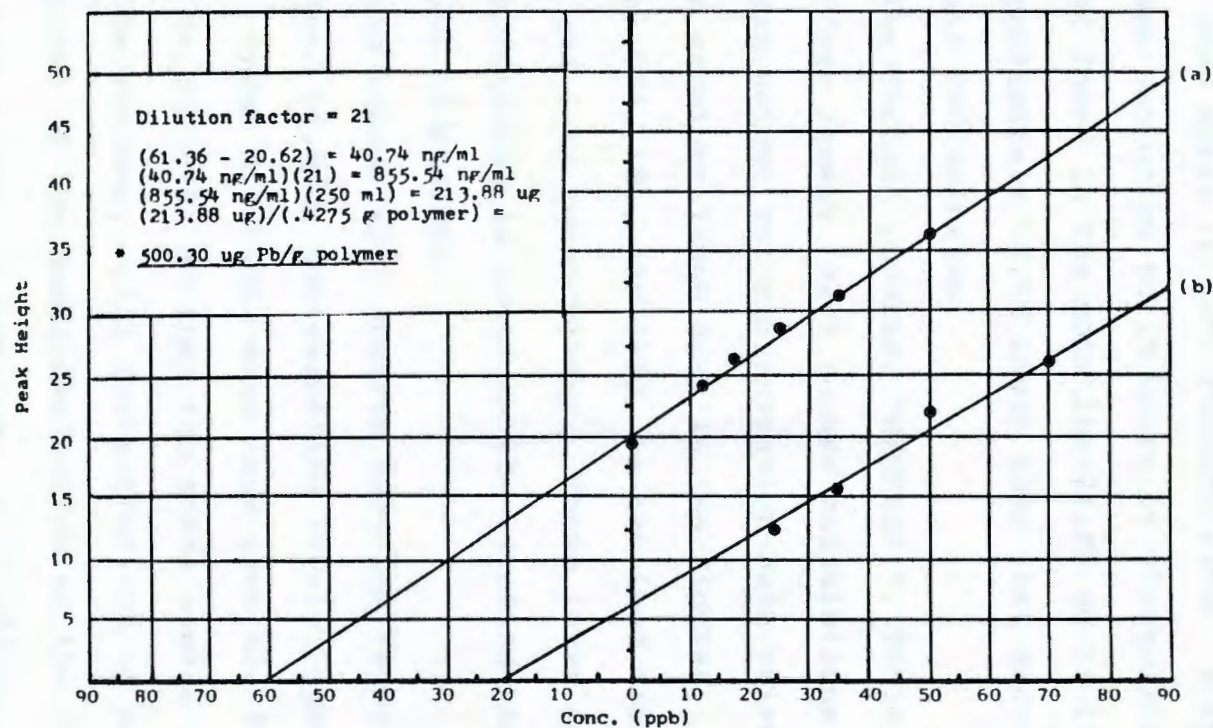
lower wavelength by as much as 30-40 mμ (W42). Since such a shift is not observed upon the comparison of these two absorption maxima, Figures (4) and (5), it is assumed that the organic precipitant was not harmed by the procedure. The discrepancy in absorption maxima between the 8-hydroxy-quinoline parent organic and the PVO can be attributed to the substitution of the vinyl (-CH-CH<sub>2</sub>-) moiety into the 5 position of the phenol ring (P69).

The extent of PVO purification with regards to lead can be followed by comparing Figures (6), (9), and (12). Each figure represents straight line extrapolations of the standard and standard addition data pairs. These data pairs were obtained through analysis by atomic absorption. Lead values found through extrapolation of these data pairs were used in the calculations accompanying each respective figure. Figure (6) indicates data pairs for standard curve (b) and the PVO solution plus a known lead spike (a). This PVO solution has not yet been electrolyzed therefore the lead level calculated here is to be considered representative of the level of lead contamination in a synthesized lot of the precipitant. Figure (9) represents data pairs for a standard curve (b) and the PVO solution plus a known spike (a). However, this PVO solution has been subjected to electrolysis for approximately 3.5 hours. The decrease in contamination is reflected in the calculated lead level found after extrapolation of these data pairs. After 3.5 hours of electrolysis the initial lead concentration was reduced from



Fig. (6) Atomic Absorption Pb <sup>+2</sup> peak height vs.  
conc. graph of the polymer solution before  
electrolysis; both std. and std. addition  
curves.

Polymer Solution Before Electrolysis  
(Pb<sup>2+</sup>)



	<u>Slope</u>		<u>Intercept</u>		<u>Corr. Coeff.</u>
Std. Addition Curve (a)	.33 +/-	.02	20.03 +/-	.43	.9957
Std. Curve (b)	.29 +/-	.02	5.91 +/-	1.24	.9927

Fig. (6)

500.30 ug of lead/ g of PVO to 219.91 ug of lead/ g of PVO or by 56%. Continued purification and analysis of the final PVO solution is represented in Figure (12). Again, data pairs for the standard curve (b) and PVO solution plus a known lead spike (a) are extrapolated. This PVO solution has been subjected to 15 hours of electrolysis and the level of lead found in the solution 21.86 ug of lead/ g of PVO, is approximately 95.6% lower than that determined in the original PVO solution.

The fortran program, "REGRESS1", Table II, was written to perform linear least square calculations and to best fit the peak height vs. concentration data pairs. This results in the straight lines seen in the figures. Peak heights for Figures (6), (9), and (12) are obtained from Figures (8), (11), and (14) respectively. These later figures represent lead absorption as found in the standard and standard addition injections.

The reader will observe dilution factors in the calculations of each contamination level, Figures (6), (9), and (12). These dilutions were made upon the PVO solutions prior to analysis so that the total acetic acid concentration could be reduced. High concentrations of acid caused "creeping" of the sample solutions up the sides of the pipet tips used to make injections. This effect prohibited representative sample analysis. However, through dilution of the sample solutions and incorporation of a dilution factor into these calculations, the problem was overcome.



Fig. (7) Polarographic scan of the polymer solution before electrolysis indicating current flow at -0.39 volts vs. SCE. This current flow is due to the reduction of  $\text{Pb}^{+2}$

# Polarographic Scan Before Electrolysis

500.32 ppb  $\text{Pb}^{+2}$  in 5 M Acetate Buffer polymer  
solution, pH = 2.5

1  $\mu\text{A}$  full scale sensitivity

2 mV/sec scan rate

Before Electrolysis

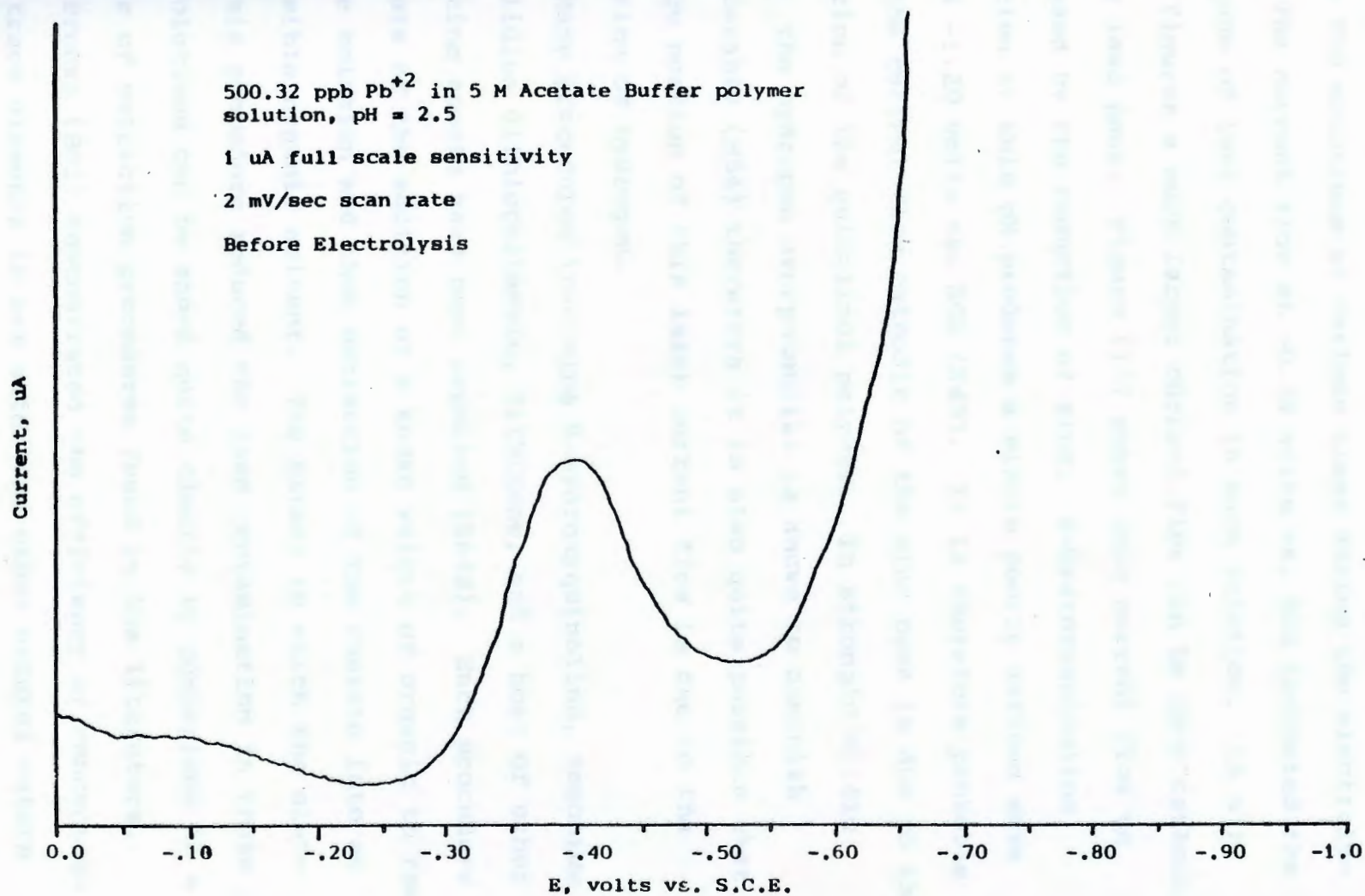


Fig.(7)

Figures (7), (10), and (13) are of polarographic scans of the PVO solutions at various times during the electrolysis. The current flow at -0.39 volts vs. SCE indicated the magnitude of lead contamination in each solution. In all three figures a much larger current flow can be seen cathodic of the lead peak. Figure (15) shows this current flow to be caused by the reduction of zinc. 8-Hydroxyquinoline reduction at this pH produces a single poorly defined wave around -1.20 volts vs. SCE (S49). It is therefore probable that the current flow cathodic of the zinc peak is due to the reduction of the quinolinol polymer. In strongly acidic media the hydrogen overpotential is known to diminish considerably (H54) therefore it is also quite possible that a large portion of this later current flow is due to the evolution of hydrogen.

Many procedures involving 8-hydroxyquinoline, ammonium pyrrolidine dithiocarbamate, dithizone, and a host of other chelating agents have been reported (S64B). Each procedure consists of the addition of a known weight of organic to the sample solution and then extraction of the chelate into an immiscible organic solvent. The extent to which the electrolysis procedure reduced the lead contamination in these PVO solutions can be shown quite clearly by comparison to a number of extraction procedures found in the literature.

Brooks (B65) demonstrated the efficiency of concentrating trace elements in sea water and other natural waters by counter-current solvent extraction. The experiment



Fig. (8) Strip chart recorder pen deflections indicating the absorption of both std. and std. addition injections. These peak heights were used for calculation of the curve in Fig. (5).

Absorption of Std. and Std. Addition Injections of  
Lead and PVO Solution Before Electrolysis

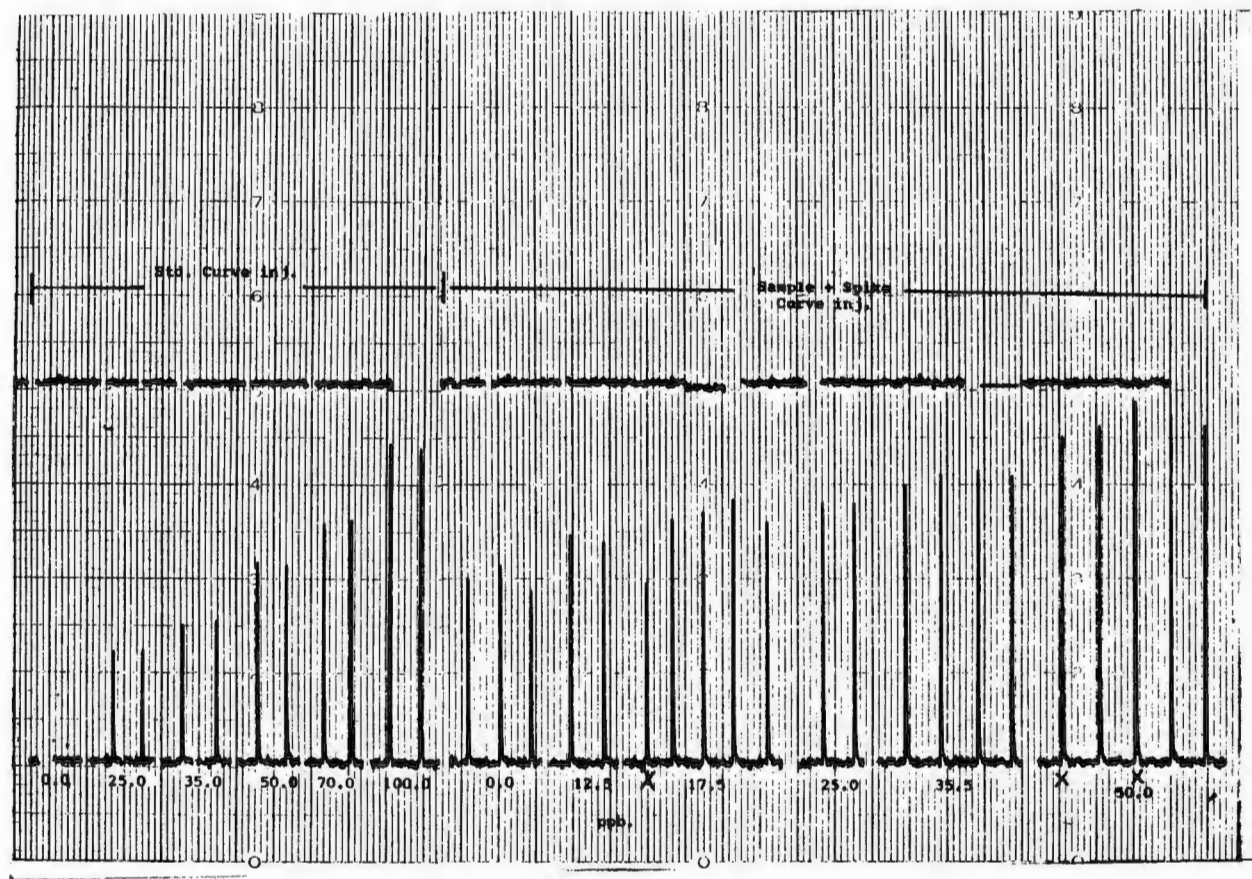


Fig. (8)

performed consisted of quantitative extraction with 1% 8-hydroxyquinoline in chloroform. Twenty milliliters of this organic mixture were added to eight liters of sea water. If non-purified PVO were used a contamination of lead amounting to 153.1 ug would have been added to the sample. Goldberg (G61) cites the estimated concentration of lead in sea water as approximately .1 ng/ml. The overall effect of this amount of PVO would have been the addition of 19.0 ng of lead to the sea water sample. This sample after quantitative extraction would have produced a total lead concentration of 819.0 ng. The extracted eight liters of sea water resulting in 800.0 ng of lead and lead contamination originating from the PVO amounting to the 19.0 ng. This yields a 2.3% error in lead level analysis. Use of purified PVO would have produced an error of approximately .125%.

The Surgeon General's report (S70) on childhood blood lead poisoning defines the clinical significance of blood lead levels. A blood lead level of 0.39 ug/ml whole blood is considered normal, 0.4-0.49 ug/ml is suggestive of undue lead absorption, 0.5-0.79 ug/ml reflects a possible case of lead poisoning, and 0.8 ug/ml or above is considered an unequivocal case of poisoning.

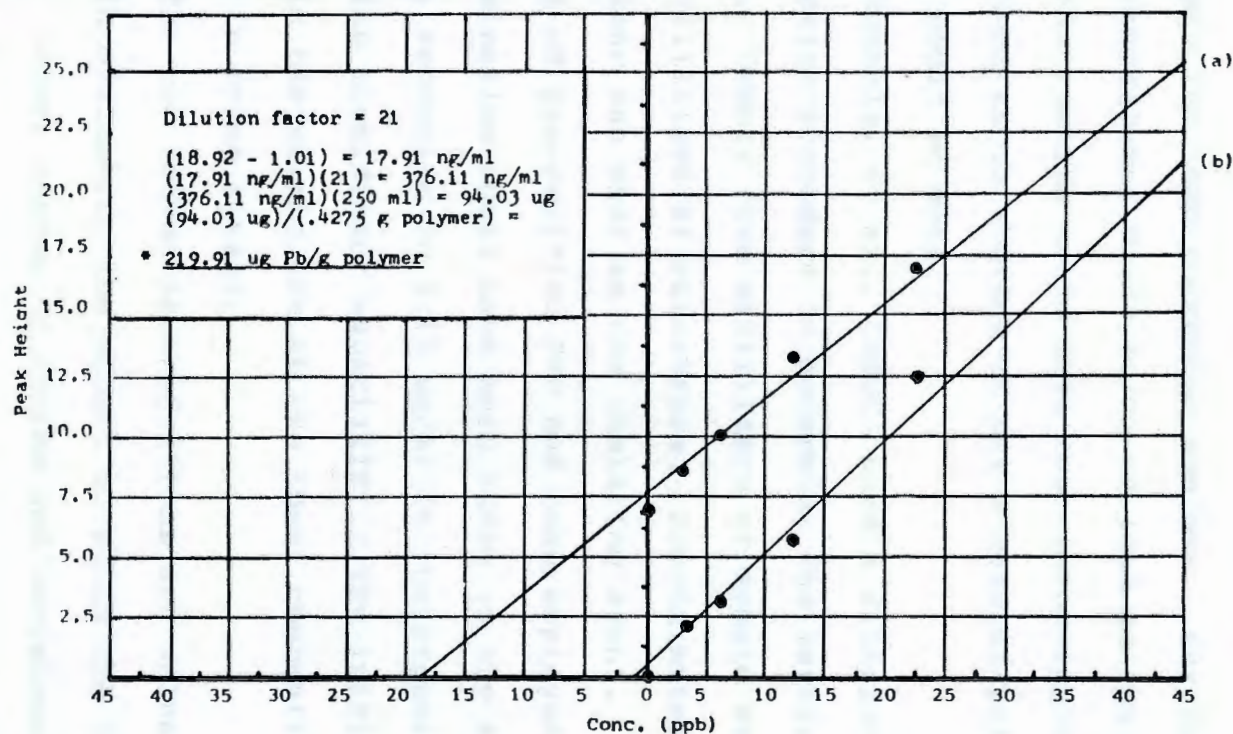
Mitchell, et al., (M72A) describes a procedure for the determination of lead in whole blood using Triton X-APDC (ammonium pyrrolidine dithiocarbamate) reagent and extracting with methyl isobutyl ketone (MIBK). The total weight of



Fig. (9) Atomic Absorption  $Pb^{+2}$  peak height vs.  
conc. graph of the polymer solution after  
3.5 hrs. of electrolysis; both std. and  
std. addition curves.

Polymer Solution After 3.5 hrs. of Electrolysis

(Pb<sup>2+</sup>)



	Slope	Intercept	Corr. Coeff.
Std. Addition Curve (a)	.39 +/- .02	7.45 +/- .31	.9947
Std. Curve (b)	.42 +/- .01	.43 +/- .17	.9995

Fig. ( 9 )

APDC added to 1 ml of whole blood was approximately 0.008 g. An equivalent weight of nonpurified PVO would have contributed around 4.0 ug/ml of lead contamination to these samples. This level of lead would have rendered these analysis for lead poisoning useless. Purified PVO would have contributed 0.175 ug/ml of lead to the samples. Again, analysis results would have been inconclusive; however, a statement as to whether or not a case of poisoning did indeed exist could be made.

Roosels, et al., (R68C) used a dithizone-chloroform extraction procedure to determine the levels of lead in urine. Twenty five milliliters of sample were extracted into ten milliliters of chloroform. Approximately 0.003 g of dithizone was used as the chelating agent. If an equivalent weight of pre-purified PVO had been employed, 1.5 ug of lead contamination would have been added to the sample. This level, amounting to 0.15 ug/ml in the organic extract phase is quite significant especially if the initial levels of lead in the sample are at the lower concentration range found in urine (S64A).

The two latter determinations are valuable diagnostically in evaluating the extent to which the body has absorbed lead. Future course of action and decisions will be influenced by the lead concentrations reported. Concentrations of both essential and non-essential trace metals in human body fluids and tissues are routinely monitored and changes are observed in a variety of disease conditions (S75, S73, W73).



Fig. (10) Polarographic scan of the polymer solution after 3.5 hrs. of electrolysis indicating reduced  $\text{Pb}^{+2}$  conc. in comparison to Fig. (7).

# Polarographic Scan After 3.5hrs. of Electrolysis

219.885 ppb  $\text{Pb}^{+2}$  in 5 M Acetate Buffer polymer  
solution, pH = 2.5

1  $\mu\text{A}$  full scale sensitivity

2 mV/sec scan rate

Electrolyzed for 3.5 hrs. at -.80 volts vs. S.C.E.

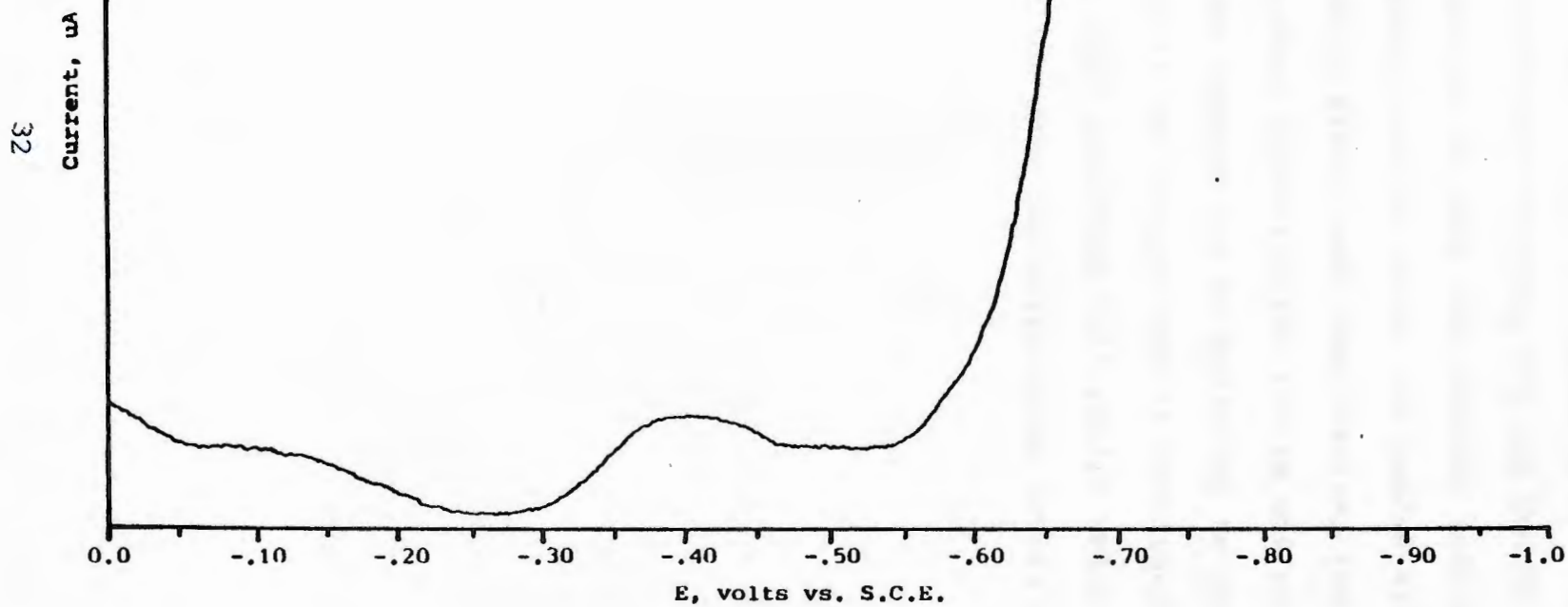


Fig. (10)

Although this purification procedure was successful in removing a good percentage of lead contamination from the PVO, 15 hours of electrolysis obviously did not remove enough of the contamination to make this reagent useful in clinical analysis. Where precise values are needed with such responsibility being placed upon the results, the PVO still contains high enough contamination levels not to be reliable. However, the reagent can be subjected to longer electrolysis times and if the proper care is exercised in recovery and storage, this procedure will purify unlimited quantities of reagent for even the ultra-trace levels of analysis.



Fig. (11) Strip chart recorder pen deflections indicating the absorption of both std. and std. addition injections. These peaks were used for calculation of the curve in Fig. (9).

Absorption of Std. and Std. Addition Injections of  
Lead and PVO Solution After 3.5 hrs. of Electrolysis

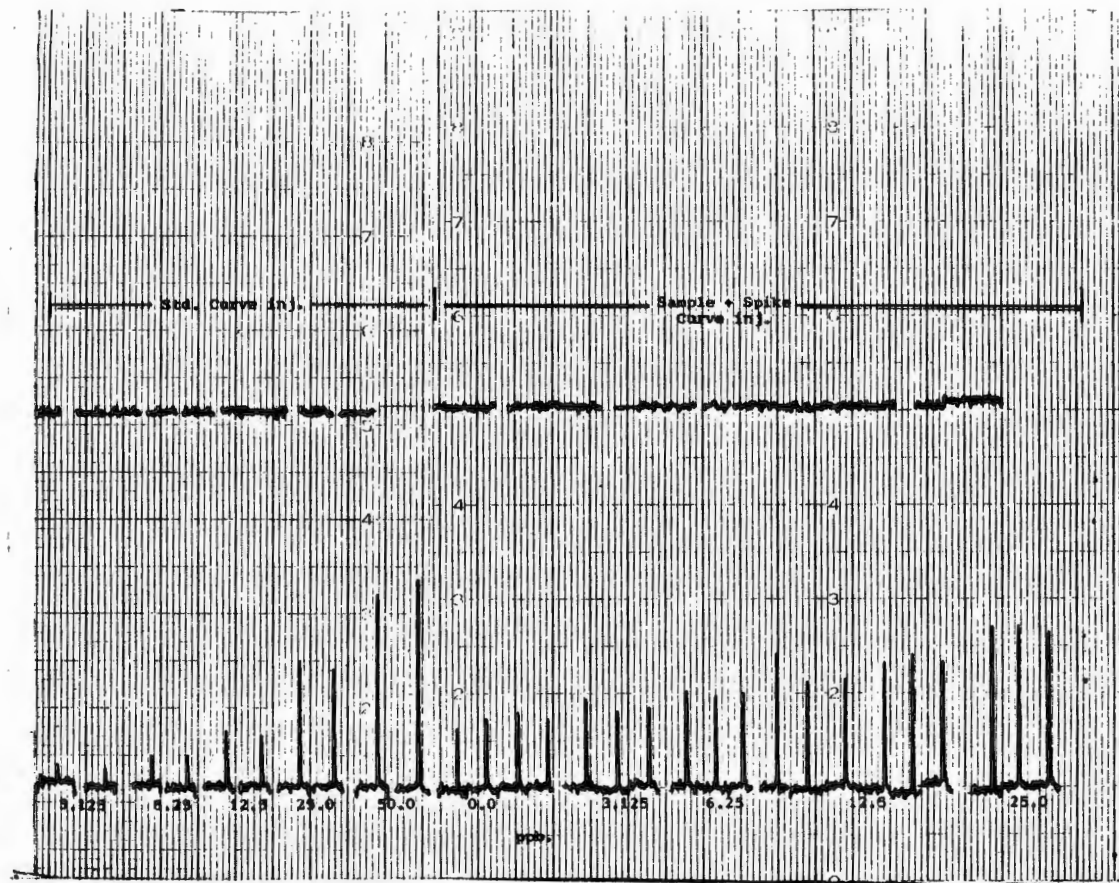


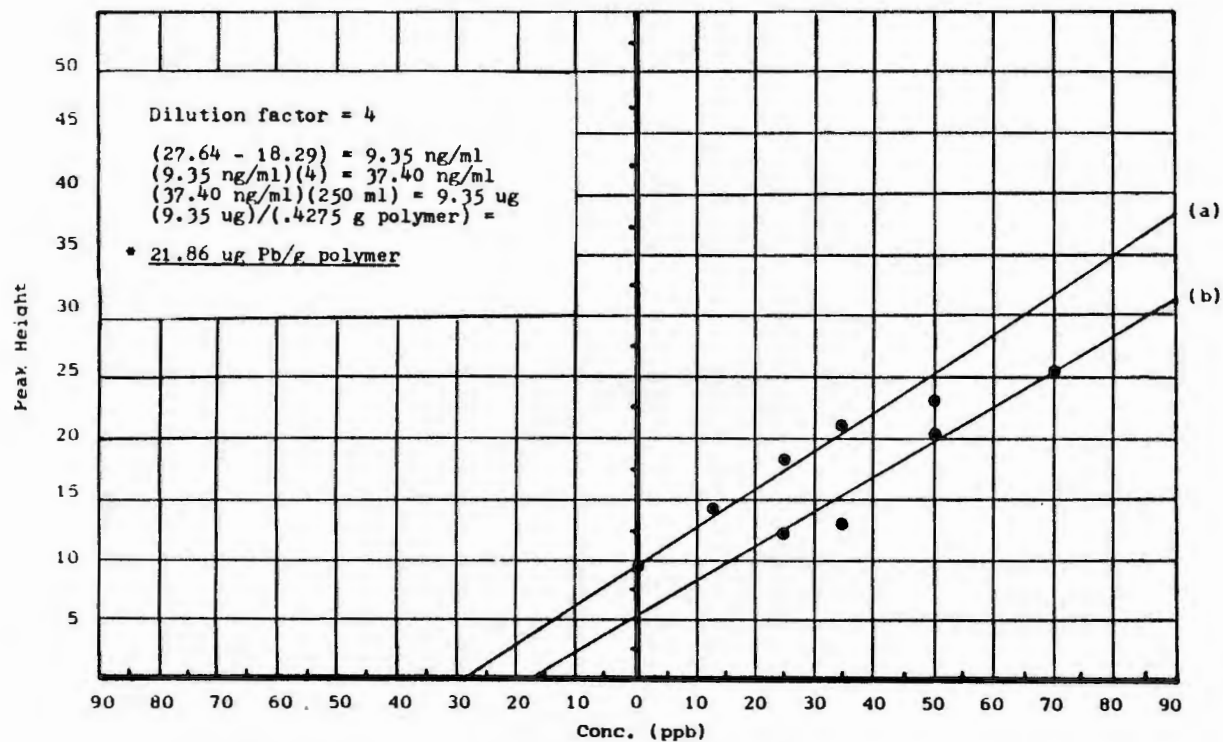
Fig. (11)

Fig. (12) Atomic Absorption  $\text{Pb}^{+2}$  peak height vs.  
conc. graph of the polymer solution after  
15 hrs. of electrolysis; both std. and  
std. addition curves.



Polymer Solution After 15 hrs. of Electrolysis

(Pb<sup>2+</sup>)



	<u>Slope</u>	<u>Intercept</u>	<u>Corr. Coeff.</u>
Std. Addition Curve (a)	.34 +/- .02	9.35 +/- .46	.9965
Std. Curve (b)	.28 +/- .02	5.14 +/- .01	.9891

Fig. (12)

Fig. (13) Polarographic scan of the polymer solution after 15 hrs. of electrolysis indicating even further reduction in the  $\text{Pb}^{+2}$  conc. in comparison to Fig. (10).

# Polarographic Scan After 15hrs. of Electrolysis

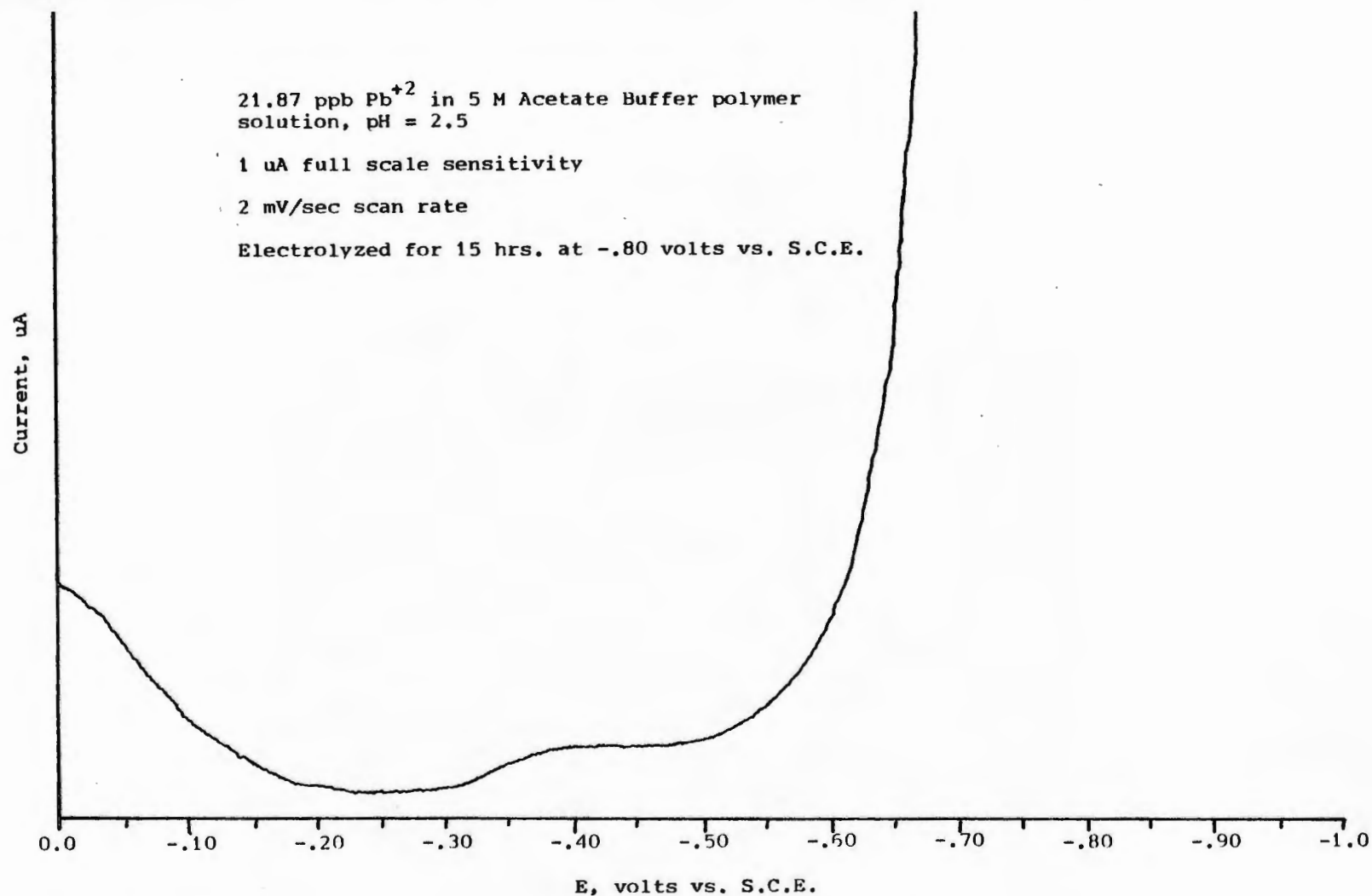


Fig. (13)



Fig. (14) Strip chart recorder pen deflections indicating the absorption of both std. and std. addition injections. These peak heights were used in calculation of the curves in Fig. (12).

# Absorption of Std. and Std. Addition Injections of Lead and PVO Solution After 15 hrs. of Electrolysis

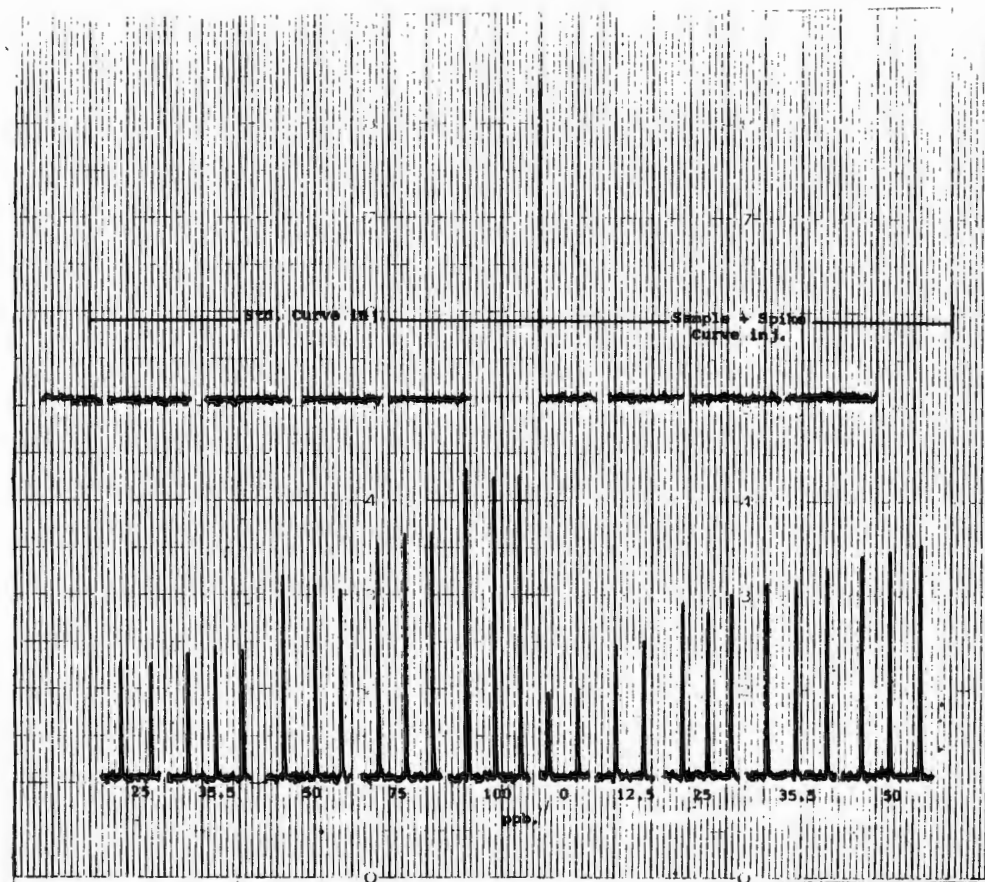


Fig. (14)

Fig. (15) Polarographic scan of the polymer solution indicating current flow at approximately -1.08 volts vs. SCE; Zinc.

note: Large contamination of the polymer solution was attributed to Zinc. In comparison to Fig. (7), Fig. (10), Fig. (13), the sensitivity of this scan is reduced by a factor of 50.



# Polarographic Scan Indicating Current Flow due to Zinc.

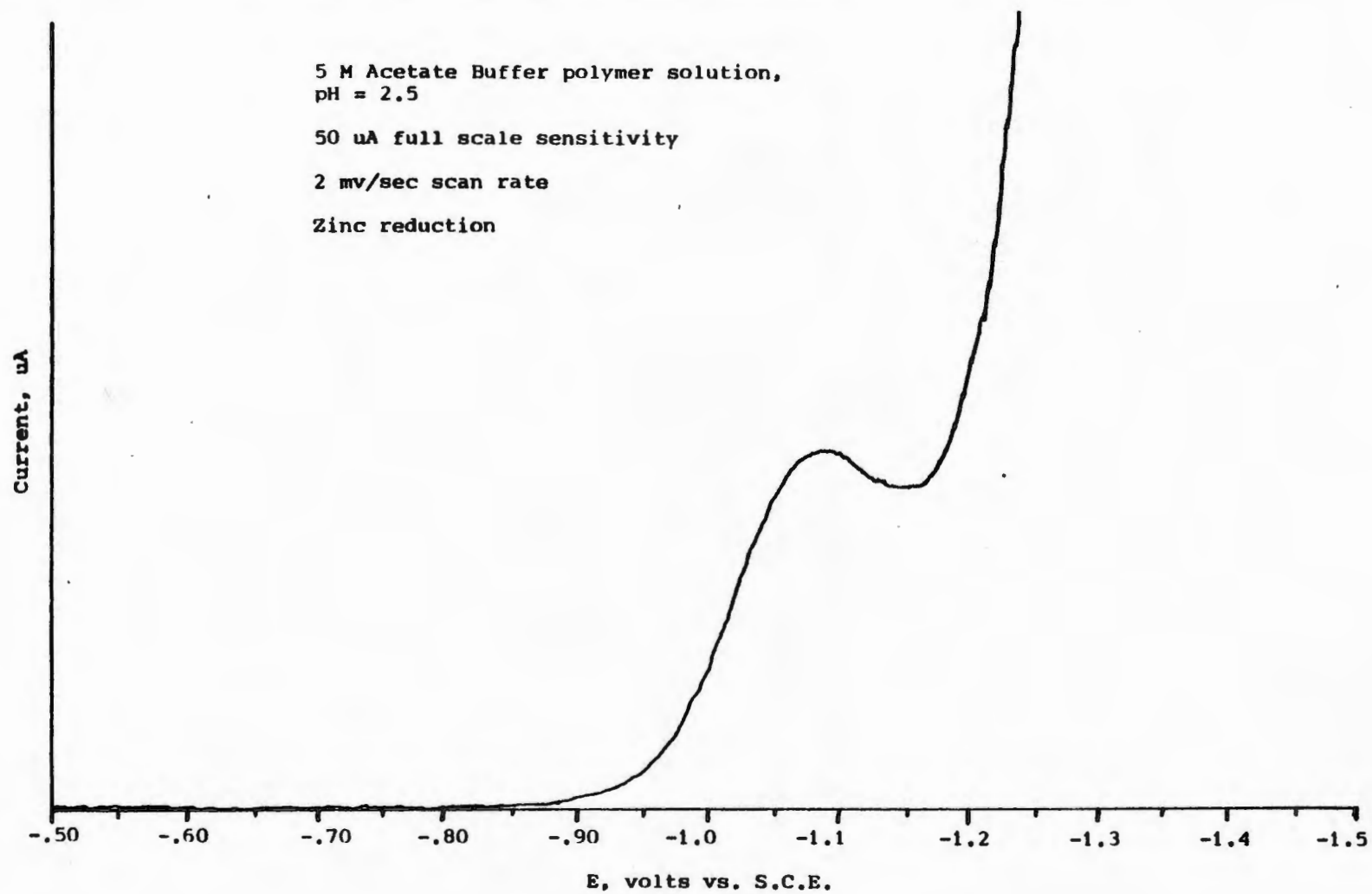


Fig.(15)

TABLE (II)

Fortran program "REGRESS1" written to do linear least square fit of the peak height vs. conc. points and to calculate slope, correlation coefficients, and intercepts along with associated statistics.

# Table (II)

REGRESS1 13:14 SAT 02 AUG 80

```

100  DIMENSION Y(25),X(25),ICARD(5)
110  WRITE(6,2)
120  READ(5,3)ICARD
130  WRITE(6,4)
140  READ(5,*) N
150  WRITE(6,5)
160  READ(5,6)SON
170  IF(N-2) 7,7,8
180  8WRITE(6,9)N
190  DO 10 I=1,N
200  READ(5,*) X(I),Y(I)
210 10CONTINUE
220  GO TO 11
230  7STOP
240 11CONTINUE
250  WRITE(6,12) ICARD
260 12FORMAT(/2X,'ANALYSIS = ',5A4)
270  CALL LINFIT (X,Y,N,SON)
280  2FORMAT(2X,'ANALYSIS?')
290  3FORMAT(5A4)
300  4FORMAT(2X,'NO# DATA PAIRS?')
310  5FORMAT(2X,'STD CORR?')
320  6FORMAT(F 6.4)
330  9FORMAT(2X,'ENTER',I2,' DATA PAIRS/CONC-PK HEIGHT')
340  END
350  SUBROUTINE LINFIT (X,Y,N,SON)
360  DIMENSION Y(15),X(15),S(15)
370  DO 13 I=1,5
380 13S(I)=0.0
390  DO 14 I=1,N
400  S(1)=S(1)+X(I)
410  S(2)=S(2)+Y(I)
420  S(3)=S(3)+X(I)*Y(I)
430  S(4)=S(4)+X(I)*X(I)
440 14S(5)=S(5)+Y(I)*Y(I)
450  THETA=N*S(3)-S(1)*S(2)

```



# Table (II)

cont.

```

460 PHI=N*S(4)-S(1)*S(1)
470 CHI=N*S(5)-S(2)*S(2)
480 B=THETA/PHI
490 A=(S(2)-B*S(1))/N
500 V2=(CHI/N-((THETA*THETA/(N*N))/(PHI/N)))/(N-2)
510 SB=SQRT(ABS(V2*N/PHI))
520 SA=SQRT(ABS(V2*S(4)/PHI))
530 RHO=ABS(THETA/SQRT(PHI*CHI))
540 WRITE(6,15) A,SA
550 WRITE(6,16) B,SB
560 WRITE(6,17) RHO
570 WRITE(6,18)
580 WRITE(6,19)
590 DO 21 I=1,N
600 Z=A+B*X(I)
610 DIFF=Y(I)-Z
620 21WRITE(6,20) I,X(I),Y(I),Z,DIFF
621 VAL=A/B
622 VCC=VAL-SON
623 IF(VCC.EQ.0.0)GO TO 26
624 GO TO 22
625 26VCC=0.0
630 22CONTINUE
631 WRITE(6,27)SON
632 WRITE(6,28)VAL
633 WRITE(6,29) VCC
640 RETURN
641 27FORMAT(2X,'STD. CORR: = ',F7.4)
642 28FORMAT(2X,'SAMPLE PPB = ',F7.4)
643 29FORMAT(2X,'CORR. SAMPLE PPB = ',F7.4//)
650 15FORMAT(//2X,'FOR Y = A+B*X, A= ',E13.5,' +/- ',E10.3)
660 16FORMAT(2X,' AND B= ',E13.5,' +/- ',E10.3)
670 17FORMAT(2X,'AND THE CORRELATION COEFFICIENT IS ',E13.5)
680 18FORMAT(//2X,T24,'PK HEIGHT',T38,'PK HEIGHT')
690 19FORMAT(2X,'I ',T12,'CONC',T24,'OBSERVED',T38,'CALCULATED',T57,'DIF
F'//)
700 20FORMAT(1X,I2,1X,4E15.5)
710 STOP
720 END

```

## APPENDIX A

### Poly-5-Vinyl-8-Hydroxyquinoline Synthesis

Scaled-up synthesis (3x) following the route developed by Vijayaraghaven (V68) was undertaken in order to produce a good supply of the reagent. The first reaction in the synthesis of PVO involves the formation of an ester at the phenolic group. Upon the addition of aluminum chloride, the acyl group migrates from the phenolic oxygen to the 5 position of the ring. The reaction is called the Fries rearrangement and is a variation of the direct Friedel-Crafts acylation of aromatics. This reaction is most crucial to PVO yields as it is not quantitative. Upon rearrangement, the acyl group is directed by the hydroxyl group to both the ortho and para positions in the phenol ring. To increase the yield of para substituted product the temperature must be kept below room temperature. Preferably as low as 0-10C.

In an early paper by Calloway (C37), he reported that in the attempted synthesis of acetophenone from benzene and acetyl chloride in the presence of aluminum chloride that drastic and prolonged reaction conditions and especially the use of an insufficient proportion of aluminum chloride tended to encourage condensation of ketones formed in the reaction. He further stated that such a reaction involving the evolution of hydrogen chloride gas cannot be deemed complete simply by the end of gas evolution. Hydrogen

chloride gas is continually evolved during the reflux. Therefore, the completion of the reaction must be determined experimentally.

Vijayaraghaven used a 3:1 mole ratio of aluminum chloride to the reactants, acetyl chloride and oxine. Since the aluminum chloride acts as a Lewis acid, enough must be present in the reaction mixture to interact with the nitrogen in the pyridine ring of the oxine, the hydroxy oxygen, and with the attacking acetyl group. One attempted synthesis of the five acetyl compound utilizing a 2:1 aluminum chloride to reactants ratio resulted in non-recoverable tar-like products. It is assumed that condensation similar to that described by Calloway took place.

Vijayaraghaven decided the reaction was at or nearing completion after 24 hours of refluxing at 68-70C. In an attempt to discover the absolute relationship between the molar ratios present in the reaction mixture and the completion of the reaction at this temperature, several preliminary small scale reactions were performed. Whereas Vijayaraghaven's initial procedure called for 4.4 moles of aluminum chloride to 1.5 moles of oxine and 1.6 moles of acetyl chloride with a dark brown solution resulting at the end of the stated reflux time and temperature, a reaction mixture consisting of 1.1 moles of aluminum chloride and .34 moles of reactant organics resulted in a dark brown solution at the end of approximately seven hours. This mixture was allowed to continue refluxing for an additional eight hours.



At the end of this time, the solution had changed to a buff colored sludge. Further, attempts at hydrolyzation and hence precipitation of the 5-acetyl oxine resulted in separation of solvent but with the organics remaining miscible in the aqueous phase.

Prolonged reflux time using 9 moles of aluminum chloride and 3 moles each of reactants yielded the desired dark brown reaction mixture after approximately  $2\frac{1}{2}$  days. Attempts to recover the 5-acetyloxine from the solutions when the reflux time was as long as 7 days were non-reproducible. The results were extremely poor yields of the product to non-recoverable oil-like phases that had to be discarded.

From the behavior of these reaction mixtures and the results obtained, it can be assumed that a simple scale-up or scale-down of Vijayaraghaven's reaction and, therefore, the reactant molar ratios is not linear with respect to reaction completion. On the contrary, extended reaction times of the scale-down synthesis using his time for refluxing, significantly decreased the yield of the ketone product. Since aluminum chloride is such a reactive metallic catalyst, large scale synthesis utilizing this compound is extremely hard to optimize. Use of nitrobenzene as a solvent also results in a reduction in the catalytic ability of the aluminum chloride. Therefore, a determination of the effects of aluminum chloride vs. the volume of nitrobenzene used in the solvent mixture is also a consideration in



## APPENDIX B

### Potentiostat Construction

The potentiostat (D72) consists of five operational amplifiers (OA), Fig. (16), #20-#24, all of which perform a unique function. The first amplifier and surrounding circuitry, #20, makes up the ramp generator. This circuit is a simple RC integrator whose constant input voltage can be varied between 0 and  $\pm 15V$ . This is accomplished through adjustment of variable resistor #1, Fig. (44) and Fig. (47). The purpose of this circuitry is to supply a linearly varying d.c. voltage to the remainder of the board. With a capacitor of 10uF situated in the control loop of this amplifier, and resistors of 10M, 5M, 2.5M, 1M, 500K, and 250K situated at the inverting input of the amplifier, a board voltage of 5V is required to obtain scan ramps of 0.05, 0.1, 0.2, 0.5, 1.0, 2.0V/sec. respectively. The output of this RC circuit is returned to zero by closing a reset switch which discharges the 10uF feedback capacitor.

The second OA, Fig. (16), #21, functions in the circuitry which sets the potential at which the voltage ramp initiates. This amplifier is set up as a current follower producing an output voltage that is proportional to the sum of the currents entering the inverted input. By incorporating input resistors between the various voltage sources (d.c. ramp generator, initial potential setting source, and



the miscellaneous input circuit) and the amplifiers summing point, the point at which the feedback loop enters the inverted input of the amplifier, simple summing of current input from each of these circuits occurs. Since the feedback resistance and the various input resistors are all the same value (100K), a simple sum results.

The third OA, Fig. (16), #24, is a potentiometric voltage follower. The reference electrode in the electrochemical cell is connected to the inverting input of this amplifier. The auxiliary electrode is connected to the amplifier output and the output signal voltage of amplifier #21 is connected to the non-inverting input. If the voltage sensed by the reference electrode, feedback loop to the inverted amplifier input, does not equal the summed voltages entering the non-inverting input, then the amplifier output voltage will be automatically driven to a potential to compensate for the difference. This "three electrode" capability overcomes resistance due to the cell solution and electrolyte, and minimizes potential drift.

The fourth amplifier, #22, is a current voltage converter (current follower). The working electrode of the electrochemical cell is connected to the inverting amplifier input. The non-inverting amplifier is connected to common. The amplifier feedback loop contains an eight position switch by which the current flow must pass through one of the eight precision load resistors. This results in output of designated sensitivities.

Finally, the fifth OA, #23, completes the total potentiostat circuit. It functions as a voltage follower and is part of the instruments damping circuitry. A simple RC low pass filter circuit allow for a choice of 0.1, 1.0, and 5.0 sec.time constants.

The tables included in this appendix are, for the most part, self-explanatory. Tables III, IV, and V are circuit connection lists in conjunction with Figures (19), (21), and (22) respectively. Table VI is a complete component list of the potentiostat with component functions in relation to individual instrument circuits. Table VII describes the control functions found on the face plate, Figure (22), and Table VIII presents a step-by-step procedure for determining operating problems with the instrument and for calibrating the ramp generator circuit.

Fig. (16) Electronic schematic of the Potentiostat indicating the layout of resistors, capacitors, and operational amplifiers.



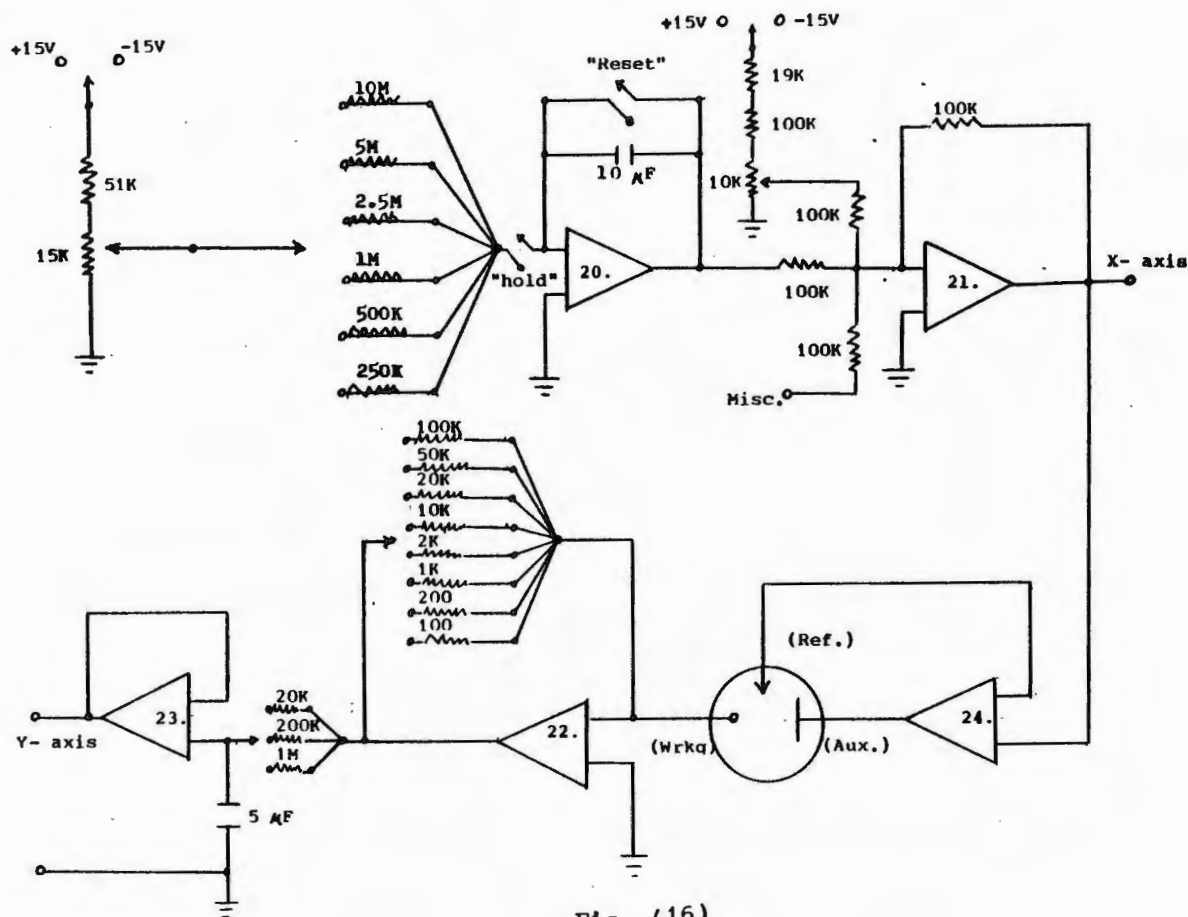


Fig. (16)

Fig. (17) Circuit connections made between components on the board as distinguished from those connections made between board components and extraneous components.

Components shown:

(8) 51 K, 5% resistor

(9,10, 11, 12, 13, 14, 19) 100 K, 1% resistors

(20,21,22,23, 24,) Fairchild UAF356/A operational amplifiers

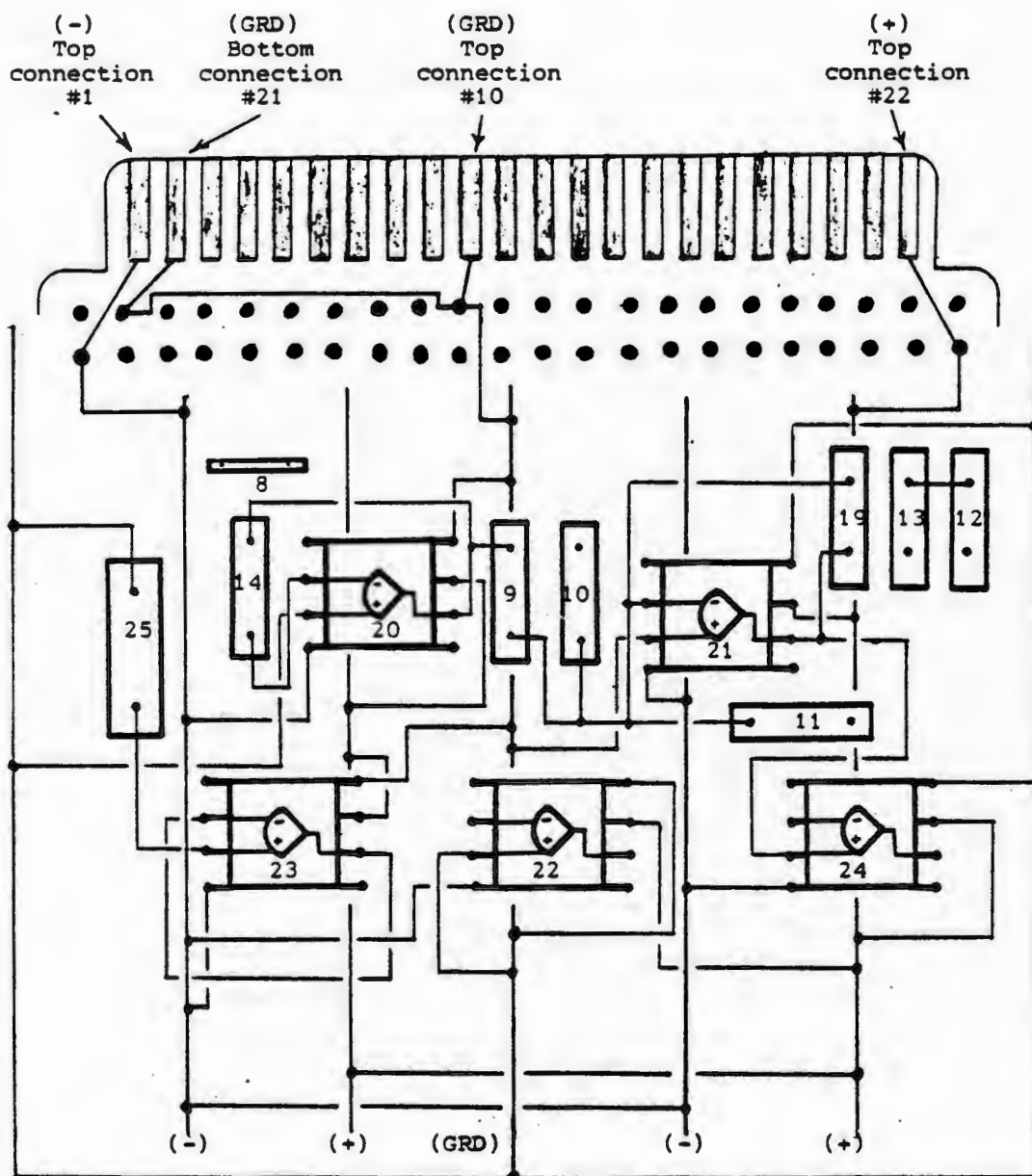


Fig. (17)



Fig. (18) Circuit connections made between the components on the board and the top edge (pins 1-22) of the connector strip.

Components shown:

(8) 51 K, 5% resistor

(9,10,11,12,13,14,19) 100K, 1% resistors

(20,21,22,23,24) Fairchild UAF356/A operational amplifiers

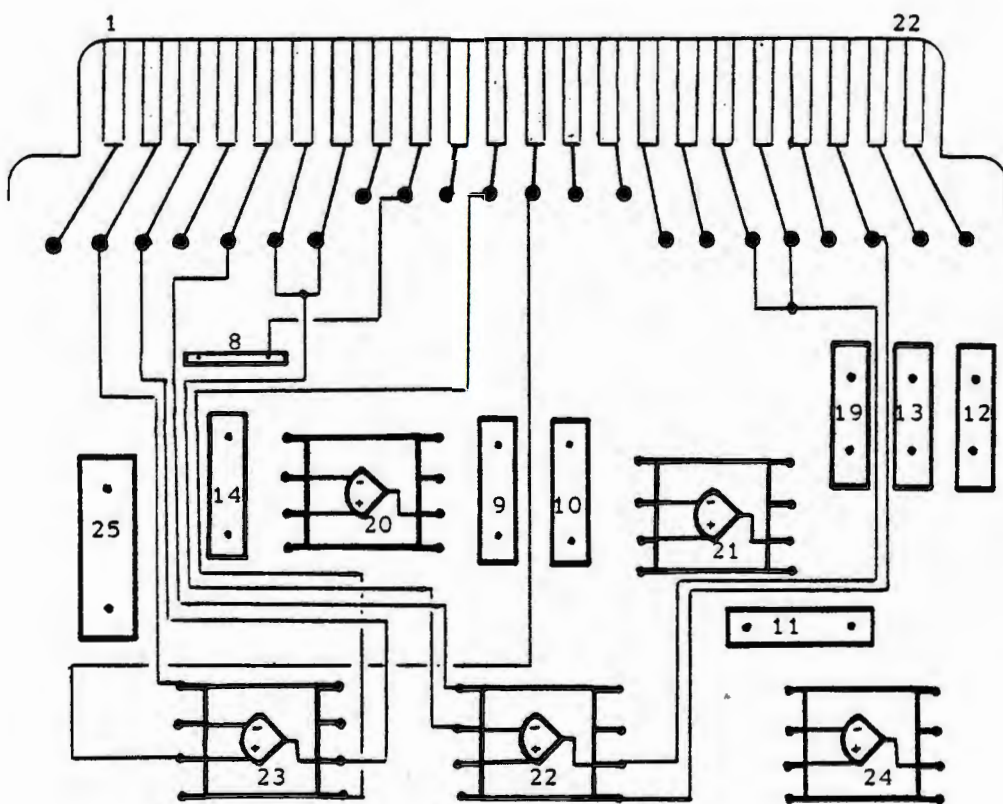


Fig. (18)

Fig. (19) Circuit connections made between the top edge (1-22) of the connector strip receptacle and the extraneous components not found on the board.

Components shown:

- (1,2,3,4,5,6,7) 10 K, Bournes variable resistors
- (27) Working electrode jack
- (28) Counter (auxiliary) electrode jack
- (29) Reference electrode jack
- (30) Y-axis jack (to recorder)
- (31) Ground jack (to recorder)
- (32,33,34,35,36,37,38) Test probe jacks
- (39) Miscellaneous voltage input jack
- (40) X-axis (b.n.c.) jack



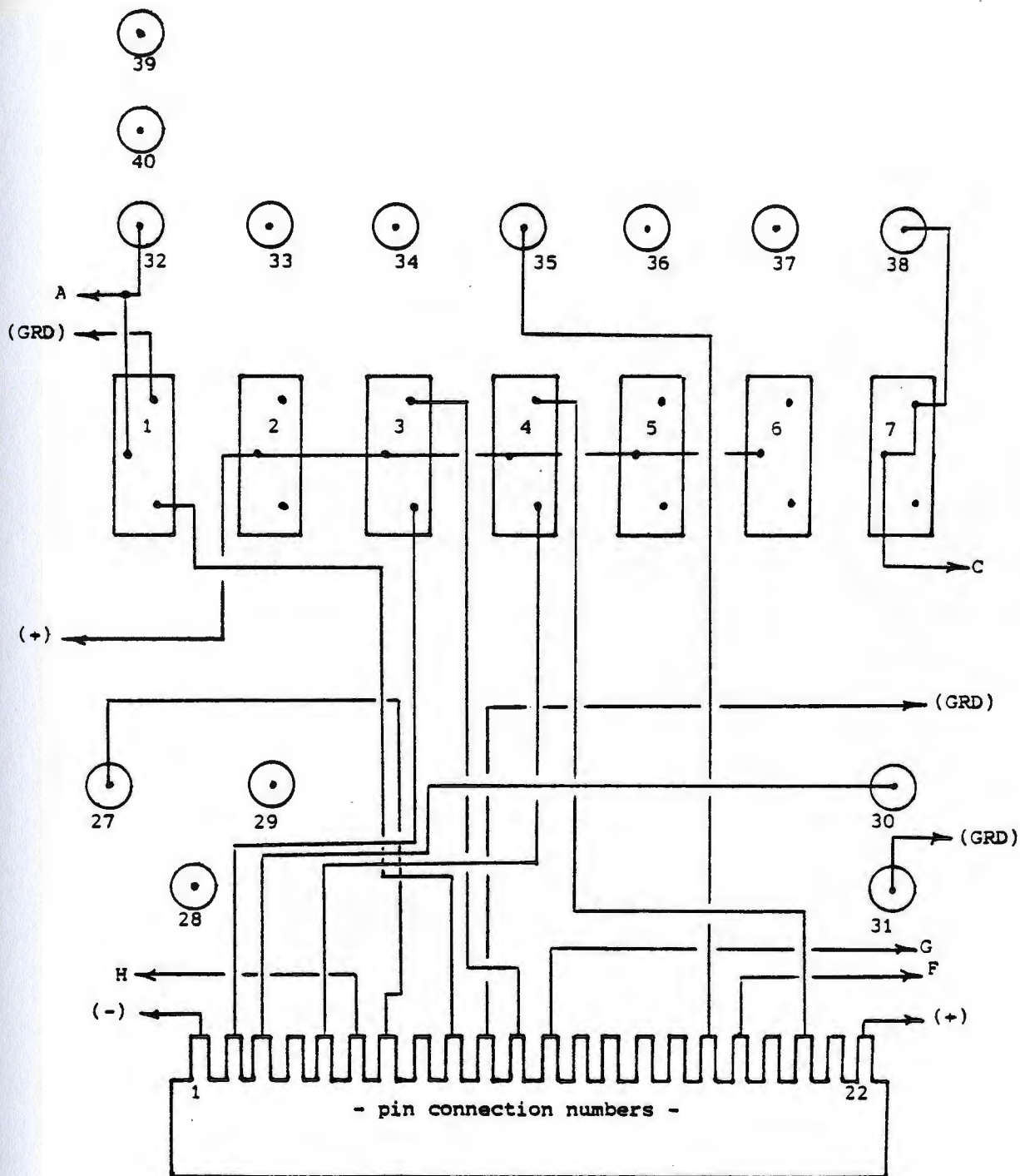


Fig. (19)

Table III

The Potentiostat Circuitry Connections Originating  
from the Top Side of the Circuit Board and Individual  
Destinations.

Table III

CIRCUIT BOARD - TOP

PIN #

- (1) Negative board connection
- (2) Connection #1 of op-amp #23 to lower pin of trimpot #3
- (3) Connection #6 of op-amp #23 to test jack #30
- (4) .....
- (5) Connection #1 of op-amp #22 to lower pin trimpot #4
- (6) Connection #2 of op-amp #22 to Full Scale Current Selector #54
- (7) Connection #2 of op-amp #22 to test jack #27
- (8) .....
- (9) Resistor #8 to lower pin of trimpot #1
- (10) Ground Connection to board
- (11) Connection #5 of op-amp #23 to upper pin of trimpot #3
- (12) Connection #3 of op-amp #23 to dampening selector #51
- (13) .....
- (14) .....
- (15) .....
- (16) .....
- (17) Connection #6 of op-amp #22 to test jack #35
- (18) Connection #6 of op-amp #22 to dampening selector #51
- (19) .....
- (20) Connection #5 of op-amp #22 to upper pin of trimpot #4
- (21) .....
- (22) Positive board connection



Fig. (20) Circuit connections made between the components on the board and the bottom edge (pins 22-1) of the connector strip.

Components shown:

(8) 51 K, 5% resistor

(9,10,11,12,13,14,19) 100 K, 1% resistors

(20,21,22,23,24) Fairchild UAF356/A operational amplifiers

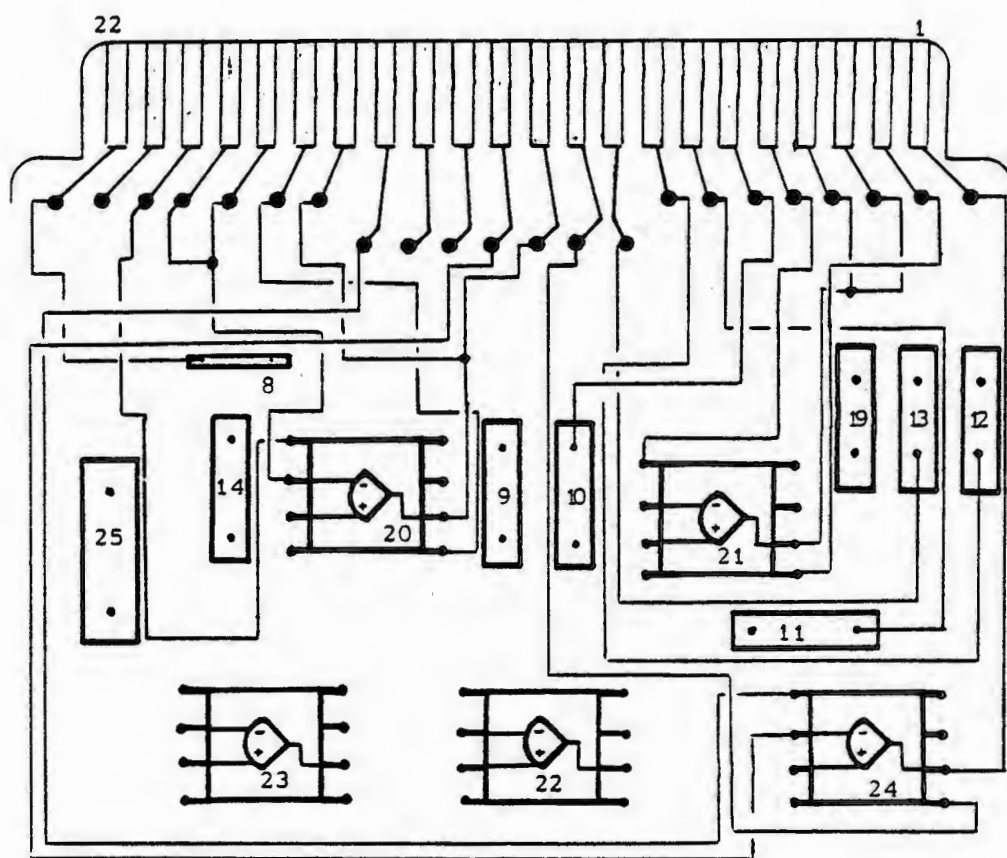


Fig. (20)

Fig. (21) Circuit connections made between the bottom edge (22-1) of the connector strip receptacle and the extraneous components not found on the board.

Components shown:

- (1,2,3,4,5,6,7) 10 K, Bournes variable resistors
- (27) Working electrode jack
- (28) Counter (auxiliary) electrode jack
- (29) Reference electrode jack
- (30) Y-axis jack (to recorder)
- (31) Ground jack (to recorder)
- (32,33,34,35,36,37,38) Test probe jacks
- (39) Miscellaneous voltage input jack
- (40) X-axis (b.n.c.) jack

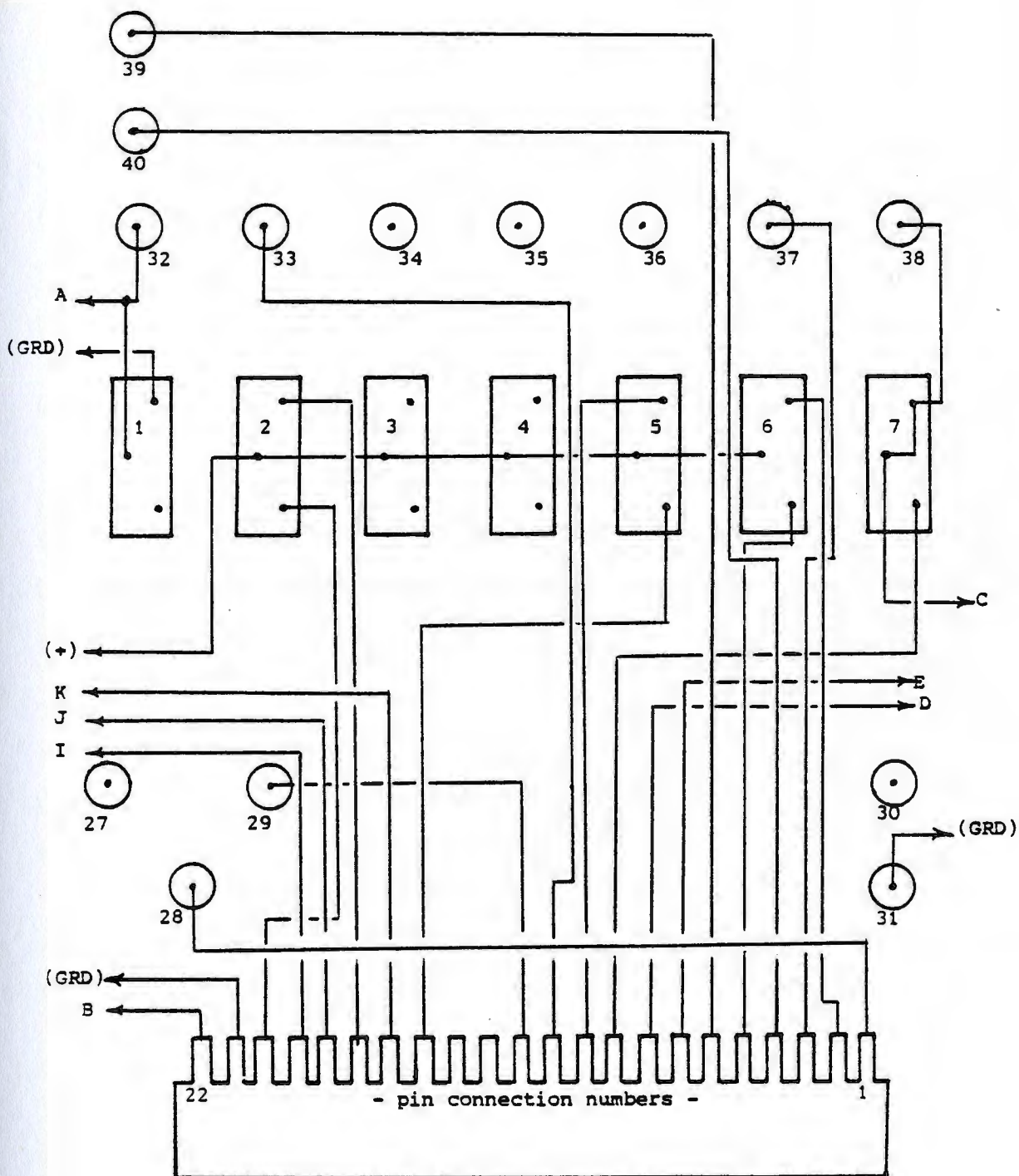


Fig. (21)



Table IV

The Potentiostat Circuitry Connections Originating  
from the Bottom Side of the Circuit Board and Individual  
Destinations.

TABLE IV

CIRCUIT BOARD - BOTTOM

PIN #

- (1) Connection #6 of op-amp #24 to Counter Electrode Jack #28
- (2) Connection #5 of op-amp #21 to upper pin of trimpot #6
- (3) Connection #6 of op-amp #21 to test jack #37
- (4) Connection #6 of op-amp #21 to b.n.c. connector #40
- (5) Connection #1 of op-amp #21 to bottom pin of trimpot #6
- (6) Resistor #10 to b.n.c. connector #39
- (7) Resistor #11 to bottom of ten turn Clarostat resistor #53
- (8) Resistor #12 to center pin of Initial Potential Polarity switch #50
- (9) Resistor #13 to lower pin of trimpot #7
- (10) Connection #5 of op-amp #24 to upper pin of trimpot #5
- (11) Connection #6 of op-amp #20 to test jack #33
- (12) Connection #2 of op-amp #24 to test jack #29
- (13) .....
- (14) .....
- (15) Connection #1 of op-amp #24 to lower pin of trimpot #5
- (16) Connection #6 of op-amp #20 to upper pin of Scan Reset switch #45
- (17) Connection #5 of op-amp #20 to upper pin of trimpot #2
- (18) Connection #2 of op-amp #20 to lower pin of Scan Hold switch #46
- (19) Connection #2 of op-amp #20 to center pin of Scan Reset switch #45
- (20) Connection #1 of op-amp #20 to lower Pin of trimpot #2
- (21) To pin #10 on circuit board TOP - Ground connection
- (22) Resistor #8 to center pin of Polarity switch #49

Fig. (22) Circuit connections made between the face plate of the potentiostat, the components on the board (as indicated in Fig. (19) and Fig. (21) and the potentiostat power supply, Fig. (23).

Components shown:

- (45) Scan reset switch
- (46) Scan hold switch
- (47) Power ON switch
- (48) Power ON indicator light
- (49) Scan polarity switch
- (50) Initial potential polarity switch
- (51) Damping selector
- (52) Scan rate selector
- (53) Initial potential selector
- (54) Full scale current selector
- (55) 5 K, Bournes variable resistor

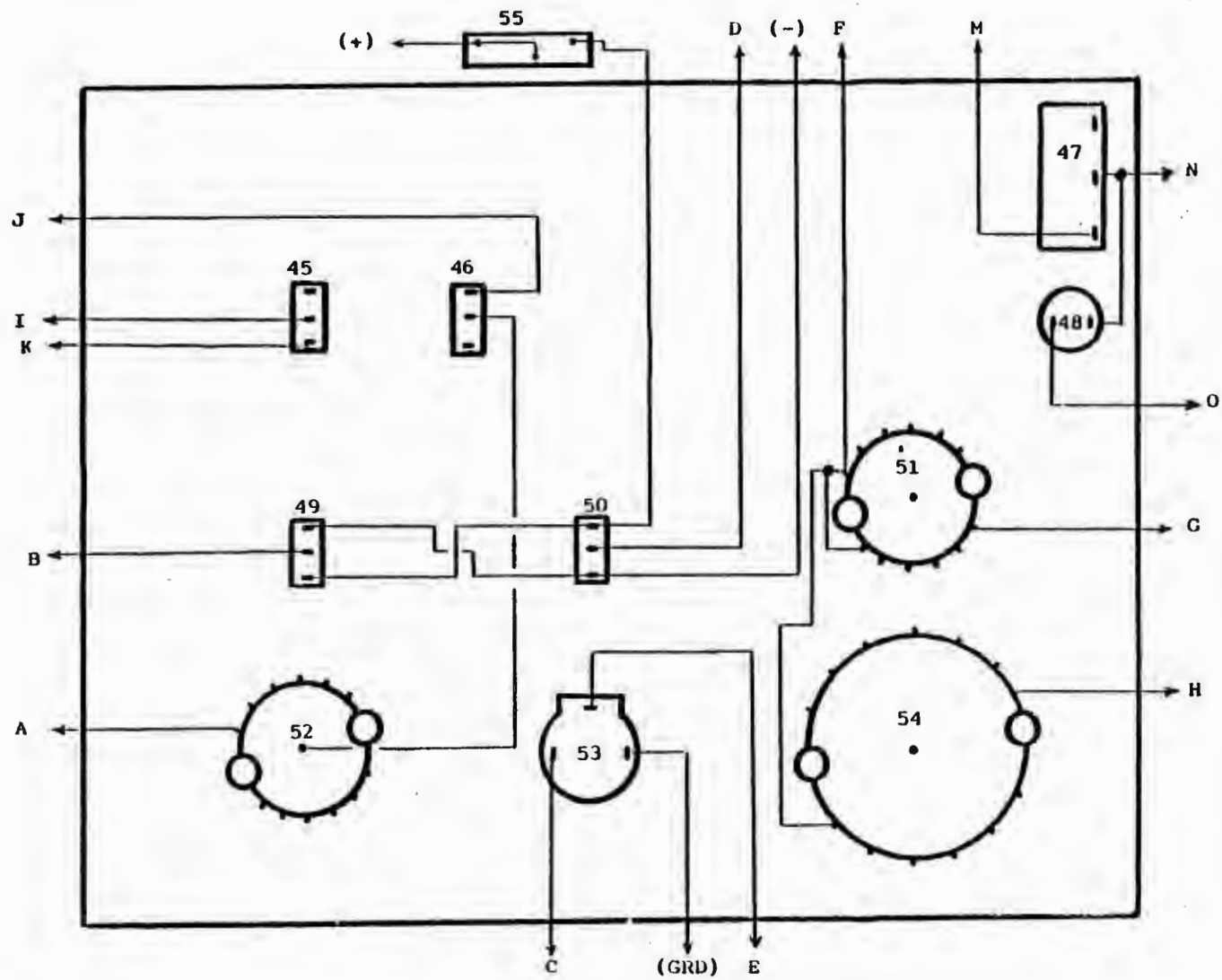


Fig. (22)



Table V

The Potentiostat Circuitry Connections Originating  
from the Face Plate and Individual Destinations.

TABLE V

- A. From the center pin of resistor (#1) to the lower ceramic base of the scan rate selector (#52).
- B. From the center pin of the scan polarity switch (#49) to resistor (#8).
- C. From the ten-turn Clarostat variable resistor to variable resistor (#7).
- D. From the center pin of the initial potential polarity switch (#50) to the 100 K resistor (#12).
- E. From resistor (#11) to the lower connection on the ten-turn Clarostat (#53).
- F. From pin 6 of amplifier (#22) to one side of the ceramic base of the damping selector (#51).
- G. From pin 3 of amplifier (#23) to the opposite side of (F) connection on the ceramic base of the damping selector (#51).
- H. From pin 2 of amplifier (#22) to the outer connection on the full scale current selector (#54).
- I. From pin 2 of amplifier (#20) to the center connection on the scan reset switch (#45).
- J. From pin 2 of amplifier (#20) to the lower connection on the scan hold switch (#46).
- K. From pin 6 of amplifier (#20) to the upper connection on the scan reset switch (#46).
- M. From the upper connection on the power ON switch (#47) to the side connection of the fuse (#56).
- N. From the center connection on the power ON switch (#47) to the back righthand connection pin of the power supply. (Fig. (23) shows the underside of the power supply.)
- O. From one of the connections on the power light indicator (#48) to the back lefthand connection pin of the power supply. (Fig. (23) shows the underside of the power supply.)

Fig. (23) Circuit connections made between the power supply, fuse, and face plate components as indicated in Fig. (22).

Components shown:

(41,42) .301 uF, Westinghouse ceramic capacitors

(43,44) 4.7 uF tantalum capacitors

(56) potentiostat fuse

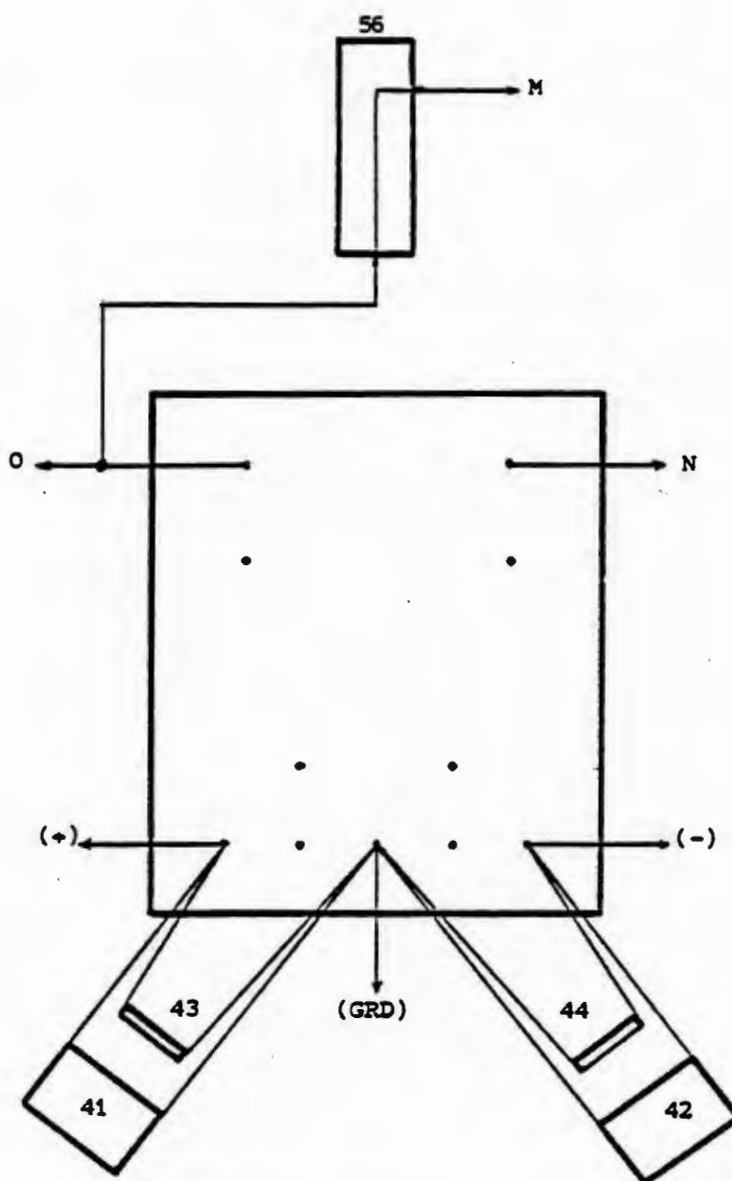


Fig. (23)



TABLE (VI)

A Complete Potentiostat Component List.

TABLE VI

COMPONENT LIST

No.

- (1) 15 K, Bournes variable resistor; functions as part of the initial voltage divider circuit between the 15 volt power supply and the ramp generator circuit.
- (2) 10 K, Bournes variable resistor; nulls the offset voltage originating from operational amplifier (#20).
- (3) 10 K, Bournes variable resistor; nulls the offset voltage originating from operational amplifier (#23).
- (4) 10 K, Bournes variable resistor; nulls the offset voltage originating from operational amplifier (#22).
- (5) 10 K, Bournes variable resistor; nulls the offset voltage originating from operational amplifier (#24).
- (6) 10 K, Bournes variable resistor; nulls the offset voltage originating from operational amplifier (#21).
- (7) 10 K, Bournes variable resistor; functions as part of the voltage divider circuit between the "initial potential" circuit and the 15 volt power supply.
- (8) 51 K, 5% resistor; functions in conjunction with (#1) as part of the voltage divider circuit between the 15 volt power supply and the ramp generator circuit.
- (9) 100 K, 1% resistor; functions as part of the "summing" circuit utilizing the voltage signal out of amplifier (#19).
- (10) 100 K, 1% resistor; functions as part of the "summing" circuit utilizing the voltage signal out of the miscellaneous input circuit.
- (11) 100 K, 1% resistor; functions as part of the "summing" circuit utilizing the voltage signal out of amplifier (#21), the initial potential circuit.
- (12) 100 K, 1% resistor; functions in the voltage divider circuit between the 15 volt power supply and the initial potential circuit.
- (13) 19 K resistor; functions in conjunction with resistor (#12) in the voltage divider circuit between the 15 volt

TABLE VI  
Cont'd.

No.

- (13) power supply and the initial circuit.
- (14) 10 uF Mallory, nonpolar capacitor; in combination with resistors on the scan rate selector (#52), functions in creating an "RC" circuit and, hence, the generation of scan rate.
- (19) 100 K, 1% resistor; functions in the summing circuit (summing circuit between signals introduced into the scan generator circuit by means of the miscellaneous input circuit and through the initial potential selector circuit.
- (20) Fairchild UAF346/A operational amplifier; functions as part of the ramp generator circuit.
- (21) Fairchild UAF356/A operational amplifier; functions as part of the initial potential selector circuit.
- (22) Fairchild UAF356/A operational amplifier; functions as part of the current-voltage converter circuit.
- (23) Fairchild UAF356/A operational amplifier; functions as part of the damping circuit.
- (24) Fairchild UAF356/A operational amplifier; functions as part of the voltage follower circuit.
- (25) 5 uF, polar capacitor; functions as part of the "RC" damping circuit.
- (27) Working electrode jack
- (28) Counter (auxiliary) electrode jack
- (29) Reference electrode jack
- (30) Y-axis jack (to recorder)
- (31) Ground jack (to recorder)
- (32) (black) Test probe jack; functions in determining the potential applied to the ramp generator circuit from the 15 volt power supply (adjustment of resistor (#1) will vary this potential).



TABLE VI  
Cont'd.

No.

- (33) (blue) Test probe jack; functions in determining the offset voltage as adjusted by resistor (#2) of the ramp generator circuit.
- (34) (green) Test probe jack; not functional.
- (35) (red) Test probe jack; functions in determining the offset voltage as adjusted by resistor (#4) of the current-voltage converter circuit.
- (36) (empty) Test probe jack; not functional.
- (37) (yellow) Test probe jack; functions in determining the offset voltage as adjusted by resistor (#6) of the initial potential selector circuit.
- (38) (black) Test probe jack; functions in determining the potential applied to the initial potential selector circuit as adjusted by resistor (#7).
- (39) Miscellaneous voltage input jack; functions as part of the "summing" circuit.
- (40) X-axis (b.n.c.) jack.
- (41) .301 uF, Westinghouse ceramic capacitor; functions in parallel with capacitor (#43) to filter out stray AC current from the 15 volt power supply.
- (42) .301 uF, Westinghouse ceramic capacitor; functions in parallel with capacitor (#44) to filter out stray AC current from the 15 volt power supply.
- (43) 4.7 uF Tantalum capacitor; functions in parallel with capacitor (#41) to filter out stray AC current from the 15 volt power supply.
- (44) 4.7 uF Tantalum capacitor; functions in parallel with capacitor (#42) to filter out stray AC current from the 15 volt power supply.
- (45) Scan reset switch; functions by setting scan potential back to zero volts applied. (Potential is also shorted out to whatever value is set by the initial scan selector dial (#53)).
- (46) Scan hold switch; this switch allows the scan to be



TABLE VI  
Cont'd.

No.

- (46) interrupted and the applied potential to be held constant at any time during a scan.
- (47) Power ON switch.
- (48) Power ON indicator light.
- (49) Scan polarity switch; indicates the potential of the ramp generated.
- (50) Initial potential polarity switch; indicates the polarity of the initial potential selector.
- (51) Damping selector; filter time constants of .1, 1.0, 5.0 seconds and off for output signal filtering.
- (52) Scan rate selector; this selector controls the potential of the ramp generator circuit.
- (53) Initial potential selector; a clorostat, ten-turn, 10 K variable resistor, this dial sets the initial potential of a scan. It has a range of 1.0 volts in either the positive or negative direction.
- (54) Full scale current selector; this selector affords 1  $\mu$ A, 2  $\mu$ A, 5  $\mu$ A, 10  $\mu$ A, 50  $\mu$ A, 100  $\mu$ A, 500  $\mu$ A, and 1 mA settings for full scale "Y" axis sensitivity.
- (55) 5 K, Bournes variable resistor; compensates for the difference in potential between the positive and negative directions of the Clarostat (#53) variable resistor. The ten-turn resistor does not exactly compliment the 10 K resistor (#7) its paired with.
- (56) Fuse.

Table VII

A Description of the Controls of the Potentiostat.

TABLE VII

Potentiostat Control Functions

1.) Potential Scan Controls

These controls determine the potential scan. They include the scan rate selector (#52) and the potential direction toggle switch (#49).

2.) Initial Potential Controls

These controls determine the initial potential at which a scan will begin. By use of the initial potential polarity switch (#50) in combination with the ten-turn Clarostat dial (#53), initial potentials from 0.0 volts to 1.0 volts in either direction may be selected.

3.) Current Range Selector

This control (#54) simply selects the full scale "Y" axis sensitivity of the instrument. In conjunction with operational amplifier (#22), this control affords the ability to vary the significance of the output voltage in terms of the working electrode current.

4.) Damping Selector

The potentiostat has a built in low-pass filter with sensitivity time constants of 0.1 sec., 1.0 sec., 5.0 sec., and off. This control (#51) allows for varying the reaction

TABLE VII  
Cont'd.

time of the fifth amplifier (#23). When in use, the low-pass filter provides some degree of smoothing and averaging; however, it also introduces some distortion into the output signal.

5.) Hold Control

A scan in progress can be interrupted at any time simply by flipping this switch (#46) to the "hold" position. This means the potential being applied by the ramp generator circuit will remain constant and the scan will not resume until this switch is on "off". At that time, the hold will end and the scan will continue. The drift is approximately 3 mV/min..



TABLE (VIII)

A Check-out Procedure for the Potentiostat.

TABLE VIII

## I Preliminary Steps

- 1.) Connect the "Y" axis output terminal (#30) and the ground output terminal (#31) to the X-Y recorder.
- 2.) Position the recorder full scale deflection switch at 100 mV.
- 3.) Set the recorder chart speed to 1.0 cm/min. (faster if higher scan rates are used (1-2 V/min.)).
- 4.) Check the potentiostat power switch (#47) and be sure that it is OFF then plug in the line cord.

## II Procedure

- 1.) Set the controls as follows...
  - Potential Scan Rate (#52)-----0.1V/min.
  - Scan Direction (#49)-----negative
  - Initial Potential Dial (#53)-----0.0 V
  - Initial Potential Polarity (#50)-----positive
  - Full Scale Current (#54)-----100 uA
  - Scan Reset Switch (#45)-----reset
  - Scan Hold Switch (#46)-----off
- 2.) Turn the power switch (#47) to ON. The power ON indicator light (#48) will come on after a few seconds.
- 3.) Adjust the recorder pen positioning controls so that the pen is located on origin ("Y" axis = 0.0, "X" axis = 0.0 ).
- 4.) Connect both the counter electrode output terminal

TABLE VIII  
Cont'd.

(#28) and the reference electrode output terminal (#29) together. Connect these leads to one side of a 10 K resistor (This resistor acts as a "dummy cell"). To the other side of the resistor, connect the working electrode output terminal (#27).

5.) Turn the recorder power switch to ON. Readjust the baseline if necessary.

6.) Flip the scan reset switch (#45) to scan. The recorder pen should begin to trace output ramp voltage. The vertical deflection of the pen at any point simply indicates the current through the "dummy cell". With the scan rate and the recorder speed specified the voltage across this "dummy cell" will reach 0.1 V at full scale. If the full scale deflection of the recorder pen does not traverse exactly 1 cm. vs. 0.1 V, adjust the voltage supplied to the ramp generator circuit by means of variable resistor (#1). This voltage adjustment with a voltmeter by grounding the common probe of the meter to test jack (#31) and inserting the other meter probe in test jack (#32). This check will assure calibration of the ramp generator circuit.

7.) Switch off the recorder, switch off the potentiostat, then remove the 10 K resistor "dummy cell". Reconnect the electrodes to the electrochemical cell.



## APPENDIX C

### Isothermal and Sub-boiling Still Design and Construction

In the analysis of trace metals (1-100 ug/g) and ultratrace metals (less than 1 ug/g) dissolution of the sample is often necessary followed by some other type of pretreatment. In most cases, it is desirable to preconcentrate the metals of interest through a precipitation procedure. This may involve the addition of large quantities of water, acid, and/or base. The amount of reagents used in most of these preconcentration steps is usually found to be several orders of magnitude greater than the amount of the original dissolved sample. This makes it essential that reagents be of the highest purity possible so as to minimize a serious source of contamination.

As the literature indicates (C52,Z76,L74), the use of high-purity commercially produced acids and bases does not assure contamination free reagents. For this reason, a study was undertaken to examine the designs of a number of isothermal and sub-boiling distillation apparatus, for possible construction and use in this laboratory.

Irving and Cox (I58) describe a very simple still for the production of "metal-free" high-purity reagents by isothermal distillation. Their still consisted of a desiccator containing technical grade acid in a pool around the bottom of the vessel. In the center of this acid pool was placed a polyethylene bottle of ultrapure water. When the



dessicator cover was replaced, distillation began. Their results showed that after 2 days at room temperature (18-20C), 2 N hydrochloric acid was obtained. In another still, under the same conditions, they obtained 9.5N ammonium hydroxide solution.

Kwestroo (K65) used a similar still for the production of ultrapure hydrofluoric acid. His system utilized all polyethylene components. Two 250 ml polyethylene beakers were placed within a polyethylene wash basin. One beaker contained technical grade hydrofluoric acid while the other contained ultrapure water. The second wash basin was inverted and set on top of the first basin. Ultrapure acid was again produced through the absorption of the acid vapors by the ultrapure water. After 2 days, at room temperature, the pure acid produced was found to be 12M. Replenishment of the starting acid was found to produce 25M ultrapure acid after an additional 2 days.

In 1972, Kuehner (K72) reported on a commercially available sub-boiling still made of quartz and a similar still he constructed entirely out of Teflon-FEP. This still consisted of a two-liter bottle through the bottom of which had been inserted a heating tube fabricated from a glass rod, a glass cold finger tube, (both were enclosed in Teflon) and the acid inlet port. Within the bottle a Teflon trough was fastened to collect condensate as it dripped off the cold finger. This condensate then flowed down the trough, out the outlet tube inserted in the bottle cap, and into

the collection bottle. The still utilized a reservoir delivery system for keeping the volume of acid within the still at a level compensating for losses through the distillation.

The chemical inertness and thermal stability of Teflon-FEP makes it ideal as material to construct an ultra-pure reagent still; however, it can be expensive and has proven hard to shape and weld in the laboratory. For these reasons Dabeka (D76) constructed a sub-boiling still out of polypropylene. His still utilized a two-quart bottle as the distillation chamber and a trough fabricated from the side of a one-quart bottle.

This work reports on the design and construction of a sub-boiling still entirely fabricated out of polyethylene and on an isothermal still similar to that which was reported by Kweestroo. Although a still constructed from polyethylene lacks the strength of one constructed entirely of polypropylene, polyethylene is able to resist attack from hot nitric acid, thereby expanding the still's capability.

#### Description and Operation

The first still set-up was similar to Kweestroo's in that two wash basins (Nalgene polypropylene, 10½ top ID x 3½ deep 4 qt.) were used to facilitate a closed environment for the distillation. Approximately 250 ml of reagent grade acid ( $\text{HNO}_3$  or  $\text{CH}_3\text{COOH}$ ) or base ( $\text{NH}_4\text{OH}$ ) was poured directly into the bottom of the upright basin. Three



polyethylene 125 ml wide mouth bottles containing ultra-pure water were set directly into the acid and positioned around the center of the upright basin.

In contrast to both of the isothermal stills described previously, a piece of polyethylene sheeting was fashioned into the shape of a cone and heat sealed to the underside of the inverted upper basin. Initial designs of this still indicated that even at room temperature condensation would sometimes form on the flat surface of the inverted upper basin. The cone-like addition eliminated the possible contaminating effects of this condensation.

Once the still was set up and the inverted basin was in place a piece of clean laboratory tygon tubing was used to fasten the top basin to the bottom basin. By slicing the required length of tubing along its length and slipping it over the top and bottom molded hand grips of the basins, a secure seal assuring a closed system was obtained. Fig. 24 presents this isothermal distillation apparatus.

The second still constructed followed the designs of Kuehner and of Dabeka. This sub-boiling still was constructed from a Nalgene (LPE) two-liter rectangular wide mouth bottle Fig. 25. The reagent inlet port, located approximately 2-2½" from the bottom of the bottle, was fabricated from a length of polyethylene tubing shaped at a right angle and a Nalgene "quick disconnect." One end of the tubing was heat welded to the quick disconnect and the other was cut to a length of about 2.5 mm above the floor of

Fig. (24) Isothermal Still

1) Nalgene, polypropylene 4 qt. basins 2) Polyethylene sheeting fashioned into a cone 3) Tygon tubing sliced down the center and fit over hand grips of basins 4) 125 ml polyethylene bottle filled with acid/base (Purified reagents were also obtained by pouring the conc. acid/base directly into bottom of the upright basin) 5) 125 ml polyethylene bottle filled with deionized water



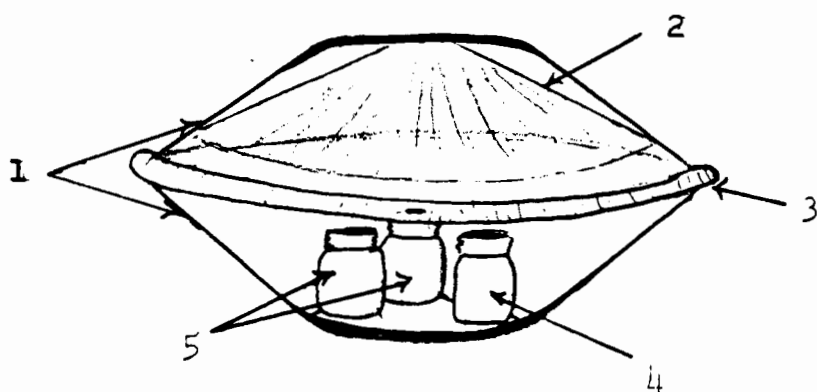


Fig. (24) Isothermal Still

Fig. (25) Sub-boiling Still

- 1) Cooling water inlet 2) Cooling water outlet
- 3) Cold finger 4) Drain carrying the purified reagent
- 5) Trough to catch the condensate 6) Reagent reservoir
- 7) Purified reagent storage bottle 8) Distillation chamber 9) Still drain

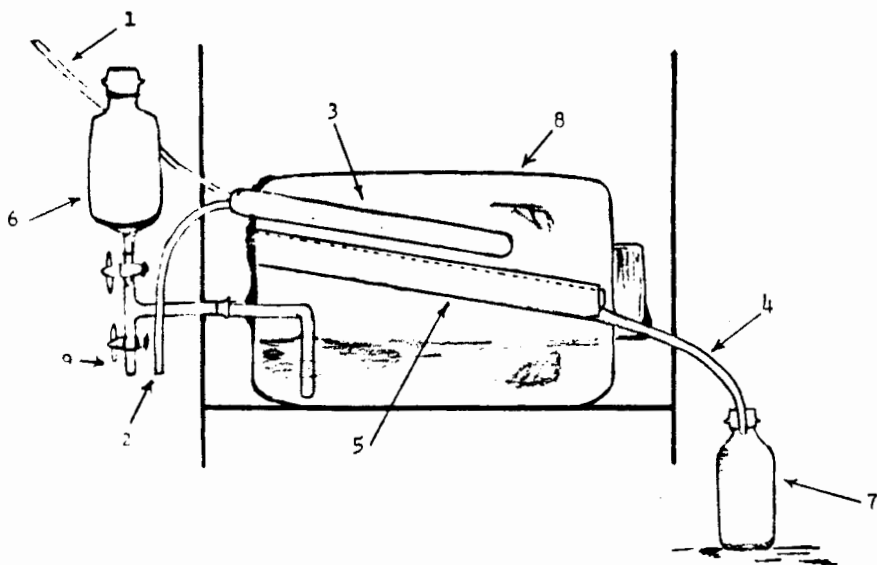


Fig. (25) Sub-boiling Still

the inside surface of the chamber. The quick disconnect was then welded to the bottom of the bottle.

Another hole was drilled into the bottom of the bottle approximately 1" from the top of the chamber. Into this hole was inserted a 3/4" (LPE) tube, sealed at one end. This functioned as a sleeve for the cold finger. This cold finger sleeve was then also welded to the bottom of the bottle.

Directly below this cold finger port a 2½" wide piece of polyethylene sheeting, previously heated and bent lengthwise at a right angle, was inserted through the bottom of the bottle. This "trough" was allowed to extend the length of the chamber to a point on center with the bottle cap and about 5 mm off the bottom of the bottle neck. The other end of the trough was then polyethylene welded to the bottom of the bottle.

The outlet tube was fashioned from a piece of 3/8" polyethylene tubing and inserted through a hole in the cap of the bottle. It was positioned so that the condensation dripping off the trough would enter the tube and pass out of the chamber into the collecting bottle.

The reservoir was constructed from a 250 ml Nalgene (LPE) narrow mouth bottle, a T-type polypropylene connector, and polyethylene tubing. Fig. 25 shows the positioning of the stopcock. In operation the bottom of the reservoir sits approximately 4½" above the distillation chamber floor. When emptying the chamber, it was found necessary to screw



the reservoir cap on tightly and start a suction out of the open drain stopcock. Once the flow of reagent from the still well was begun complete drainage of the chamber was possible.

The heat source for this apparatus was a 250W Westinghouse heat lamp. This was positioned approximately eight inches above the top of the chamber. This distance produced a temperature of 75C on the outside chamber roof. Positioning of the lamp cannot be close enough to heat up the polyethylene and soften the chamber. This would also cause the solution within to boil. The distance of the lamp to the chamber specified here proved adequate in keeping both roof and the walls of the chamber sufficiently warm enough to prohibit "climbing" of reagent and of forming condensation on any inside surfaces other than the cold finger.

Flameless atomic absorption analysis of the distillation products of  $\text{NH}_4\text{OH}$  and  $\text{CH}_3\text{COOH}$ , by both still designs, indicated substantial purification with remaining contamination at the extreme low ppb levels.

#### Preparation and Cleaning Procedure

All preparation of materials and operation of the still was carried out in a class 100 air chamber (Environmental Air Control, Inc.) on teflon coated, laminar air flow bench tops or in laminar flow benches set up in the laboratory. Leaching was carried out following the method

Karin, Bueno, and Fasching (K75). All materials were first washed with deionized distilled water then acid leached by submersion into warm (35-40C) 8N HNO<sub>3</sub> for a minimum of 72 hours. At this time, the materials were removed from the acid, rinsed many times with the deionized distilled water, and set out to dry in the laminar flow bench.

(1971) *Journal of Public Health Analysis*, *Standard Methods for the Examination of Water and Wastewater*, 13th Ed., 1971/1972.

(1973) *Journal of Public Health Analysis*, *Standard Methods for the Examination of Water and Wastewater*, 13th Ed., 1973/1974.

(1977) *Journal of Public Health Analysis*, *Standard Methods for the Examination of Water and Wastewater*, 13th Ed., 1977/1978.

(1978) *Journal of Public Health Analysis*, *Standard Methods for the Examination of Water and Wastewater*, 13th Ed., 1978/1979.

(1979) *Journal of Public Health Analysis*, *Standard Methods for the Examination of Water and Wastewater*, 13th Ed., 1979/1980.

(1980) *Journal of Public Health Analysis*, *Standard Methods for the Examination of Water and Wastewater*, 13th Ed., 1980/1981.

(1981) *Journal of Public Health Analysis*, *Standard Methods for the Examination of Water and Wastewater*, 13th Ed., 1981/1982.

(1982) *Journal of Public Health Analysis*, *Standard Methods for the Examination of Water and Wastewater*, 13th Ed., 1982/1983.

## BIBLIOGRAPHY

- (A48) Analytical Methods Committee. Metallic Impurities in Foodstuffs Sub-Committee Report No. 4, The Determination of Zinc in Foodstuffs, Analyst, 73, 304 (1948)
- (A54) Analytical Methods Committee. Report of the Lead Panel of the Metallic Impurities in Foodstuffs Sub-Committee, The Determination of Lead in Foodstuffs, Analyst, 79, 397 (1954)
- (A76) American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 14th Ed., 144(1976)
- (B65) Brooks, R. R., Liquid-Liquid, Discontinuous, Counter-Current Solvent Extraction for Determination of Trace Constituents in Geological Materials - II. Extraction with Solvents Heavier than Water, Talanta, 12, 511(1965)
- (B69) Breuier, P. G., Spencer, D. W., Smith, C. L., Determination of Trace Metals in Seawater by Atomic Absorption Spectrophotometry, Am. Soc. Test. Mater., Spec. Tech. Publ. 443, 70(1969)
- (B73) Blount, C. W., Leyden, D. E., Thomas, T. L., Guill, S. M., Application of Chelating Ion Exchange Resins for Trace Element Analysis of Geological Samples Using X-Ray Fluorescence, Anal. Chem., 45, 1045(1973)
- (B75A) Boyle, E. A., Edmond, J. M., Determination of Trace Metals in Aqueous Solutions by APDC Chelate Coprecipitation, Adv. Chem. Ser., 147, 44(1975)
- (B75B) Buono, J. A., Buono, J. C., Fasching, J. L., Rapid Precipitation of Trace Metals from High Saline Matrices by Poly-5-Vinyl-8-Hydroxyquinoline, Anal. Chem., 47, 1926(1975)
- (B78) Bosserman, P., Sawyer, D. T., Differential Pulse Polarographic Determination of Molybdenum at Parts-per-Billion Levels, Anal. Chem., 50, 1300(1978)
- (C37) Calloway, N. O., Green, L. D., Reactions in the Presence of Metallic Halides; Unsaturated Ketone Formation as a Side Reaction in Friedel-Crafts Acylations, J. Am. Chem. Soc., 59, 809(1937)



- (C52) Coppola, P.P., Hughes, R.C., Polyethylene Still for Preparation of Pure Hydrofluoric Acid, Anal. Chem., 24, 768(1952)
- (C64) Catherino, H., Meites, L., Polarographic Determination of Manganese, Anal. Chim. Acta, 23, 57(1964)
- (C66) Campbell, W.J., Spano, E.F., Green, T.S., Micro and Trace Analysis by a Combination of Ion Exchange Resin-Loaded Papers and X-Ray Spectrography, Anal. Chem., 38, 987(1966)
- (C74A) Chau, Y.K., Lum-Shue-Chen, K., Determination of Labile and Strongly Bound Metals in Lake Water, Water Res., 8, 383(1974)
- (C74B) Copeland, T.R., Osteryoung, R.A., Elimination of Copper-Zinc Intermetallic Interferences in Anodic Stripping Voltammetry, Anal. Chem., 46, 2093(1974)
- (C74C) Copeland, T.R., Skogerboe, R.K., Anodic Stripping Voltammetry, Anal. Chem., 46, 1257A(1974)
- (D72) Diefenderfer, J. A., Principles of Electronic Instrumentation, W.B., Saunders Co., Phila., Pa., 550(1972)
- (D76) Dabeka, R.W., Mykytiuk, A., Berman, S.S., Polypropylene for the Sub-boiling Distillation and Storage of High-Purity Acids and Water, Anal. Chem., 48, 1203(1976)
- (E70) Erdey, L., Polas, L., Chalmers, R.A., Development and Publication of New Gravimetric Methods of Analysis, Talanta, 17, 1143(1970)
- (F37) Fleck, H. R., The Precipitation of Metals by Means of 8-Hydroxyquinoline (Oxine), Analyst, 62, 378(1937)
- (G46) Galen, E.W., Steck, E.A., Absorption Spectra of Heterocyclic Compounds. I. Quinolinols and Isoquinolinols, J. Am. Chem. Soc., 68, 2181(1946)
- (G61) Goldberg, E.D., Marine Geochemistry, Ann. Rev. Phys. Chem., 12, 29(1961)
- (G76) Going, J.E., Wesenberg, G., Preconcentration of Trace Metal Ions by Combined Complexation - Anion Exchange Part I., Anal. Chim. Acta, 81, 349(1976)
- (H53) Heggen, G.E., Strock, L.W., Determination of Trace Elements, Anal. Chem., 25, 859(1953)



- (H54) Hollinshead, R. G. W., Oxine and its Derivatives, 1, 19(1954), Butterworths Scientific Publ., London
- (H75) Hasebe, K., Osteryoung, J., Differential Pulse Polarographic Determination of Some Carcinogenic Nitrosamines, Anal. Chem., 47, 2412(1975)
- (I58) Irving, H., Cox, J. J., The Preparation of Metal-Free Acids, Alkalies, and Buffer Solutions of High-Purity, Analyst, 83, 526(1958)
- (K61) Kublik, Z., Application of the Hanging Drop Mercury Electrode for Determination of Traces of Copper, Lead, and Cadmium in Waters, Acta Chim. Acad. Sci. Hung., 27, 79(1961)
- (K65) Kwestroo, W., Visser, J., The Ultrapurification of Hydrofluoric Acid, Analyst, 90, 297(1965)
- (K72) Kuehner, E. C., Alvarez, R., Paulsen, P. J., Murphy, T. J., Production and Analysis of Special High-Purity Acids Purified by Sub-Boiling Distillation, Anal. Chem., 44, 2050(1972)
- (K75) Karin, R. W., Buono, J. A., Fasching, J. L., Removal of Trace Metal Impurities from Polyethylene by Nitric Acid, Anal. Chem., 47, 2296(1975)
- (K77) Krishnamurty, K. V., Reddy, M. M., Tris(pyrolidine dithiocarbamate)Cobalt(III) Chelate Matrix for Trace Metal Preconcentration from Aqueous Solutions by Co-precipitation, Anal. Chem., 49, 222(1977)
- (L64) Luke, C. L., Ultratrace Analysis of Metals with a Curved Crystal X-Ray Milliprobe, Anal. Chem., 36, 318(1964)
- (L74) Little, K., Brooks, J. D., Notes on the Preparation of Hydrochloric and Hydrofluoric Acids by the Sub-Boiling Distillation Unit of Mattinson, Anal. Chem., 46, 1343(1974)
- (L75A) Leyden, D. E., Luttrell, G. H., Preconcentration of Trace Metals Using Chelating Groups Immobilized via Silylation, Anal. Chem., 47, 1612(1975)
- (L75B) Leyden, D. E., Patterson, T. A., Alberts, J. J., Preconcentration and X-Ray Fluorescence Determination of Copper, Nickel, and Zinc in Seawater, Anal. Chem., 47, 733(1975)

- (L77) Lo, J. M., Wel, J. C., Yeh, S. J., Preconcentration of Mercury, Gold, and Copper in Seawater with Lead Diethyldithiocarbamate for Neutron Activation Analysis, *Anal. Chem.*, 49, 1146(1977)
- (M47) Mitchell, R. L., Scott, R. O., Application of Chemical Concentration by Organic Reagents to Spectrographic Analysis, *Spectrochim. Acta*, 3, 368(1947)
- (M55) Meites, L., Purification of Supporting Electrolytes for Polarographic Trace Analysis by Controlled-Potential Electrolysis at a Mercury Cathode, *Anal. Chem.*, 27, 416(1955)
- (M59) Meites, L., Moros, S. A., Background Correction in Controlled-Potential Coulometric Analysis, *Anal. Chem.*, 31, 23(1959)
- (M72A) Mitchell, D. G., Ryan, F. J., Aldous, K. M., The Precise Determination of Lead in Whole Blood by Solvent Extraction - Atomic Absorption Spectrometry, *A. A. Newslet.*, 11, 120(1972)
- (M72B) Moody, G. J., Thomas, J. D. R., Development and Publication of Work with Selective Ion-Sensitive Electrodes, *Talanta*, 19, 623(1972)
- (M73) Mark Jr., H. B., Development and Publication of New Methods in Kinetic Analysis, *Talanta*, 20, 257(1972)
- (M74) Meites, L., Zuman, P., Electrochemical Data Part (III), A, Wiley & Sons Publ. Co., N.Y. (1974)
- (P42) Piper, C. S., Investigation on Copper Deficiency in Plants, *J. Agr. Sci.*, 32, 143(1942)
- (P69) Pasto, D. J. Johnson, C. R., Organic Structure Determination, Prentice Hall, N. J., 100(1969)
- (R62) Rees, W. T., Fluorimetric Determination of Very Small Amounts of Aluminum, *Analyst*, 87, 202(1962)
- (R68A) Riley, J. P., Taylor, D., Chelating Resins for the Concentration of Trace Elements from Seawater and Their Analytical use in Conjunction with Atomic Absorption Spectrophotometry, *Anal Chim. Acta*, 40, 479(1968)
- (R68B) Robertson, D. E., Role of Contamination in Trace Element Analysis of Seawater, *Anal Chem.*, 40, 1067 (1968)



- (R68C) Roosels, D., Vanderkeel, J.V., An Atomic Absorption Determination of Lead in Urine After Extraction with Dithizone, A.A. Newslet., 7, 9(1968)
- (R73) Ramirez-Munoz, J., How to Write a Paper on Atomic Absorption Spectrometry, Talanta, 20, 705(1973)
- (R74) Rosatti, H., Design and Publication of Work on Stability Constants, Talanta, 21, 809(1974)
- (S25) Shikuta, M., The Electrolysis of Nitrobenzene with the Mercury Dropping Cathode, Trans. Faraday Soc., 21, 42(1925)
- (S49) Stock, J.T., The Polarography of Quinoline Derivatives Part II. The Reduction of 8-Hydroxyquinoline at the Dropping Mercury Cathode, J. Chem. Soc., 586(1949)
- (S64A) Slavin, W., Sprague, S., The Determination of Certain Toxicological Trace Metals by Atomic Absorption Spectrophotometry, A.A. Newslet., 3, 7(1964)
- (S64B) Stary, J., The Solvent Extraction of Metal Chelates, Macmillian Co., N.Y. (1964)
- (S70) Steinfield, J.L., Surgeon General's Policy Statement on Medical Aspects of Childhood Lead Poisoning, Public Health Service, (1970); A.A. Newslet., 11, 120(1972)
- (S73) Sunderman, W.F., Atomic Absorption Spectrometry of Trace Metals in Clinical Pathology, 4, 549(1973)
- (S74) Sinko, I., Dolizak, J., Simultaneous Determination of Copper, Cadmium, Lead, and Zinc in Water by Anodic Stripping Voltammetry, J. Electroanal. Chem., 25, 299(1974)
- (S75) Schwartz, M.K., The Role of Trace Metals in Cancer, Cancer Res., 35, 3481(1975)
- (V68) Vijayaghaven, N.V., Doctoral Dissertation, University of Rhode Island, (1968)
- (W42) Woodward, J., Structure and Absorption Spectra III. Normal Conjugated Dienes, J. Am. Chem. Soc., 64, 72(1942)
- (W69) Witnack, G.C., Sasselli, R., Anodic Stripping Voltammetry for Trace Analysis in Water, Anal. Chim. Acta, 47, 267(1969)

- (W73) Walsh, J. M., Copper Chelation in Patients with Wilsons Disease, Quart, J. of Med., New Series XLII, 167, 441(1973)
- (Z70) Zlatkis, A., Brulning, W., Bayer, E., Properties of the Chelating Polymer Poly-(Trisaminophenol-Glyoxal) in the Microanalysis of Copper, Anal. Chem., 42, 1201(1970)
- (Z76) Zief, M., Mitchell, J. W., Contamination Control in Trace Element Analysis, John Wiley & Sons, N.Y., (1976)